N-Heterocyclic Carbene Ligands for Iridium-Catalysed Asymmetric Hydrogenation

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Prof. Dr. Hans-Jakob Wirz
Dekan

to my wife Annik

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Abbreviations

3-NBA	3-nitro-benzyl alcohol (matrix for FAB-MS)
ad, adam	adamantyl
APT	attached proton test (NMR)
arom	aromatic
BAr_F^-	tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
BEMP	2-*tert*-butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-diazaphosphorin
BINAP	2,2'-bis-(diphenylphosphino)-1,1'-binaphtalin
Boc	*tert*-butoxycarbonyl
br	broad (NMR and IR)
c	concentration
CCDC	Cambridge Crystallographic Data Centre
CIF	crystallographic information file
cod	1,5-cyclooctadiene
COSY	correlation spectroscopy (NMR)
δ	chemical shift
d	doublet (NMR)
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DEPT	distortionless enhancement by polarisation transfer (NMR)
DIBAL	di-isobutylaluminium hydride
DMAP	dimethylaminopyridine
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulfoxide
ee	enantiomeric excess
EI	electron impact ionisation (MS)
ESI-MS	electrospray ionisation mass spectroscopy
FAB-MS	fast atom bombardment mass spectroscopy
FTIR	Fourier transform infra-red
HMBC	heteronuclear multiple-bond correlation (2D $^{1}H/^{13}C$ NMR)
HMQC	heteronuclear multiple quantum coherence (2D $^{1}H/^{13}C$ NMR)
Hz	Hertz
imid	imidazole
J	coupling constant
m	multiplet (NMR), medium (IR)
mc	multiplet centered (NMR)
mes	mesityl
MS	mass spectroscopy
ν	valence vibration (IR)
NHC	*N*-heterocyclic carbene

NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser enhancement spectroscopy
*o*Tol	*ortho*-tolyl
oxaz	oxazoline
PHOX	phosphinooxazoline
ppm	parts per million
PTSA	toluene-*p*-sulfonic acid
q	quartet (NMR)
*R*f	retention factor (TLC)
RT	room temperature
s	singlet (NMR), strong (IR)
sept	septet (NMR)
t	triplet (NMR)
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin-layer chromatography
TOF	turnover frequency
TON	turnover number
w	weak (IR)

Chapter 1

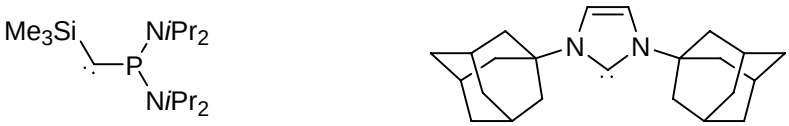
Introduction

1.1 *N*-Heterocyclic carbene (NHC)

1.1.1 Historical perspective

Since the pioneering work of Doering in 1954, carbenes have been recognised as a unique type of intermediate with characteristics distinct from radicals already known in the organic chemistry community.[1] Since then, research on carbenes has rapidly expanded, but almost no attempts were made to stabilise carbenes until the 1980s when Tomioka started to study persistent triplet diarylcarbenes.[2]

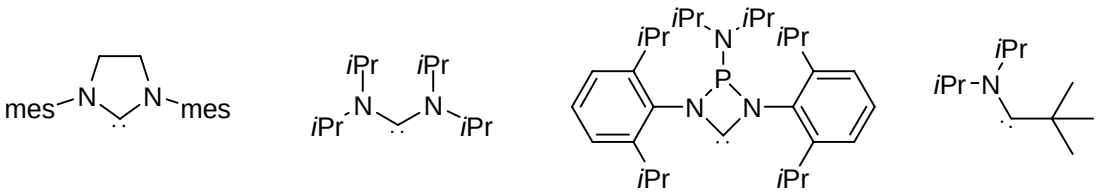
The first isolable carbenes were reported in 1988 by Bertrand[3] (**1**) and 1991 by Arduengo[4] (**2**). Phosphinocarbene **1** can be distilled at 80-85°C/10^{-2} Torr and *N*-heterocyclic carbene (NHC) **2** is a crystalline solid that melts at above 240-241°C (Figure 1.1).



1 **2**

Figure 1.1 The first isolated carbenes.

Although NHCs have been known since the pioneering work of Wanzlick, who observed their dimerisation[5] and was able to trap them to form mercury-salt carbene complexes,[6] thirty years went by before the first NHC was isolated. The particular stability of the NHCs made them very popular and during the following years further analogues were synthesised (Figure 1.2). In 1995, Arduengo proved[7] using NHC **3** that aromaticity was not needed for stabilisation, and in 1996 Alder isolated acyclic NHC **4**.[8] This research area has been continually expanded with the isolation of four-membered carbene[9] **5** by Grubbs and alkyl carbene[10] **6** by Bertrand in 2004.

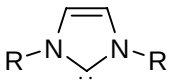


3 **4** **5** **6**

Figure 1.2 Stable NHCs and their derivatives.

1.1.2 Nomenclature

For the sake of homogeneity, the following nomenclature will be used throughout this work.[11] NHCs **7** which are related to an imidazoline structure will be called *1,3-di-R-imidazolin-2-ylidenes* and NHCs **8** with a saturated C-C double bond will be described as *1,3-di-R-imidazolidin-2-ylidenes* (Figure 1.3).



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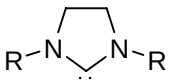

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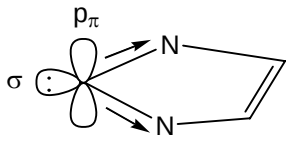
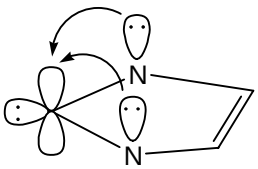
Figure 1.3 Nomenclature of the various NHCs.

1.1.3 General characteristics

Carbenes are neutral divalent carbon with only six electrons in its valence shell. With two nitrogen substituents next to the $C_{carbene}$ atom, the NHCs are predicted to stabilise their singlet state (two paired electrons in the σ orbital) by a push-pull effect (Figure 1.4).[12] Firstly, the σ-electronwithdrawing nitrogen inductively stabilises the σ-nonbonding orbital by increasing its s-character. Secondly, the energy of the vacant p_π-orbital is increased by interaction with the symmetric combination of the nitrogen lone pairs. Combination of the two effects increases the σ-p_π gap and favours therefore the singlet state. Moreover, the pseudo sp^2 hybridisation adopted by the $C_{carbene}$ atom in its singlet state matches the bent geometry of the NHC five-membered ring.



-I inductive effect



+M mesomer effect

Figure 1.4 Electronic stabilisation of NHCs.

The interaction of the nitrogen lone pair with the p_π-orbital of the carbene is reflected by a N-$C_{carbene}$ bond length of 1.365 Å, which is consistent with double bond character. An accurate assessment of the π backbonding was found by analysing dynamic ^{1}H-NMR behaviour of bis(diisopropylamine)carbene **4**.[8] As the major part of this process involves

rotation about the N-$C_{carbene}$ bonds, the measured barrier to rotation of 53 kJ/mol was mostly attributed to the substantial π-component of these bonds.

Dimerisation of NHCs has been known since the first attempts to isolate them.[5] Alder recently showed that dimerisation is thermodynamically unfavorable for imidazolin-2-ylidenes **7** (singlet/triplet gap of 354 kJ/mol), but very likely to happen for imidazolidin-2-ylidenes **8** due to lack of aromaticity and acyclic NHCs due to loss of conjugation through twisting around the N-$C_{carbene}$ bond.[13] The reaction is likely to be proton catalysed.

The ^{13}C-NMR chemical shifts[14] range from 210-220 ppm downfield from TMS for aromatic imidazolin-2-ylidenes **7**, to 235-245 ppm for imidazolidin-2-ylidenes **8** and acyclic NHCs.

1.1.4 Generation of diaminocarbene / pKa

Three principal methods were successfully used for the generation of diaminocarbenes: i) deprotonation of imidazolium salts **9** or formamidinium salts **10**, ii) desulfurisation of thioureas **11** and iii) thermolysis of methanol adducts of type **12** (Figure 1.5).

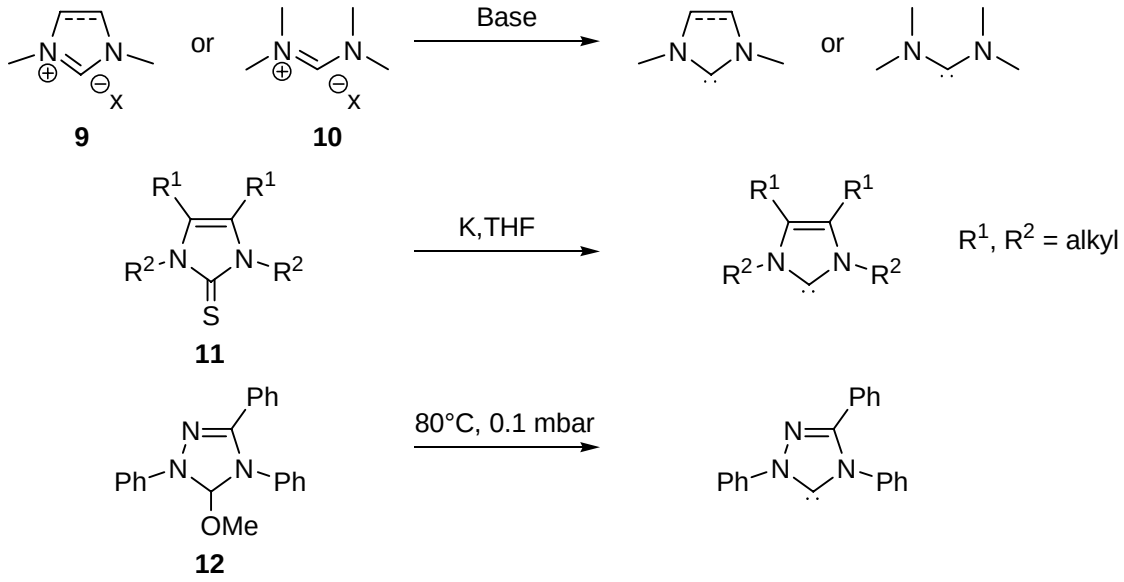


Figure 1.5 Three principal methods for the generation of NHCs.

The pKa value was measured for diisopropyl-imidazolin-2-ylidene on the DMSO scale and found to be 24 by Alder.[15,16] For di-*tert*-butyl-imidazolin-2-ylidene Streitwieser found a pKa of 20 on the THF scale.[17] Therefore, it is not surprising that the principal method used to synthesise NHCs is deprotonation of the corresponding imidazolium or formamidinium salts. For the isolation of the first NHC, Arduengo's group used NaH/KH in THF in the presence of KO*t*Bu and DMSO (to generate the dimsyl ion).[4] Herrmann showed that milder conditions

such as sodium amide in liquid ammonia and THF at -40°C, were also efficient.[18] With a pKa increased by 2 to 6 units, formamidinium salts underwent nucleophilic addition of the base rather than deprotonation.[16] This problem was solved by the use of hindered alkali amide bases such as lithium diispropylamide or potassium hexamethyldisilazide.

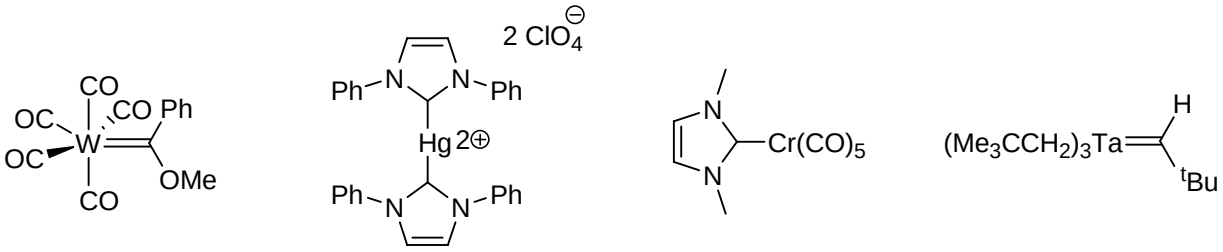
In 1993, Kuhn and Kratz reported another pathway to imidazolin-2-ylidene by reduction of the corresponding thiourea using metallic potassium.[19] This heterogeneous reaction, which has proved difficult to reproduce,[16] is attractive because the only other product is potassium sulfide which is insoluble in THF.

Finally, another successful method was established by Enders who synthesised in a good yield a triazol-2-ylidene by thermolysis of its methanol adduct.[20] One drawback of this methodology is the extreme sensitivity of the methanol adduct.

1.2 *N*-Heterocyclic carbene metal complexes

1.2.1 Historical perspective

Carbenes were introduced to inorganic chemistry by Fisher and Maasböl who reported that reaction of phenyl lithium with $W(CO)_6$, followed by addition of acid and then diazomethane, gave complex **13** (Figure 1.6).[21] A few years later Wanzlick and Öfele's first syntheses of NHC metal complexes respectively **14** and **15,** extended the Fischer type carbene family.[22,23] In 1974, Schrock developed[24] a new type of carbene, the so-called Schrock carbene, with a totally different reactivity (**16**).



13 **14** **15** **16**

Figure 1.6 Fischer, Wanzlick, Öfele and Schrock carbenes.

1.2.2 NHC ligand properties

Although the metal carbene bond in Schrock and Fischer carbene complexes are both described as double bond, they differ by the polarity of the electron density. This difference

arises from the difference in energy between the d_π orbital of the metal and the p_π orbital of the carbene (Figure 1.7). If the d_π orbital is lower in energy than the p_π orbital, the metal carbon bond is polarised δ- on the metal and δ+ on the carbene and it is a Fischer carbene complex. Contrary, if the d_π orbital is higher in energy than the p_π orbital, the metal carbon bond is polarised δ+ on the metal and δ- on the carbene and it is a Schrock carbene complex. A particular example of Fisher carbenes are NHCs which have a p_π orbital of very high energy since their multiple bonding between the carbene atom and the two nitrogen atoms. As a result, the p_π orbital does not interact well with the d_π, thus preventing almost any π-backbonding from the metal to the carbene. In the NHC complexes, the metal carbon bond is therefore best represented by a single bond.

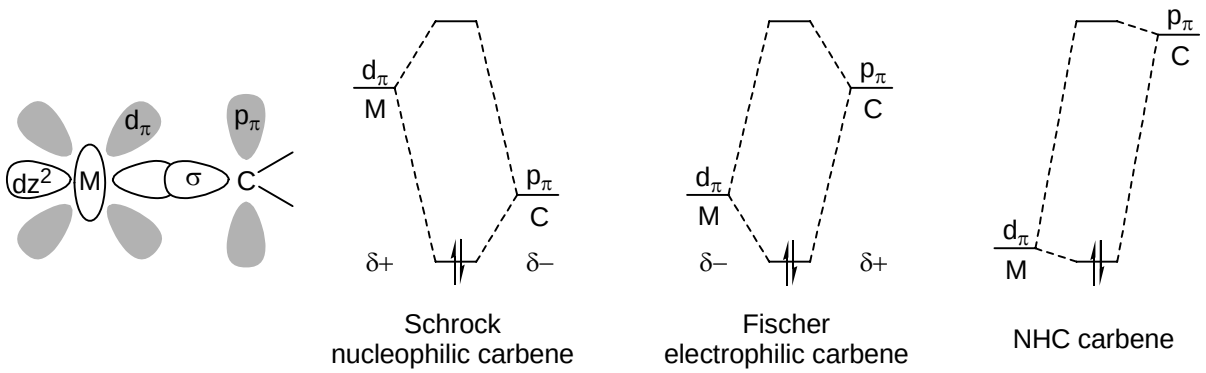


Figure 1.7 Partial molecular diagram for Schrock, Fischer and NHC carbene complexes.

The fundamental difference between a typical Schrock alkylidene moiety and an NHC as a ligand is underlined in the crystal structure of $[RuCl_2(NHC)_2(=CHC_6H_4Cl)]$ (NHC = 1,3-diisopropylimidazolin-2-ylidene) where the two types of carbenes are linked to the same metal centre.[25] The ruthenium-carbon bond of the Schrock carbene, generally written as a double bond, has a bond length of 1.821(3) Å, whereas the Ru-C bond length to the NHC (2.107(3) Å and 2.115 (3)Å) justifies its representation as a single bond (σ-donor and virtually no π-acceptor).

Measurement of IR carbonyl absorption frequencies of NHC carbonyl metal (Fe, Cr, Rh, Mo and Ir) and their phosphine analogues showed the significantly increased donor capacity of NHC relative to phosphines, even to trialkylphosphines.[26-28] Experimental investigations,[29] calorimetric studies[30,31] and experimental calculations[32] agree that the ligand dissociation energy of NHCs from Ru complexes is higher than for phosphines. Further calculations with other metals such as Au, Cu, Ag, Pd and Pt led to similar conclusions.[33,34]

By analogy to the cone angle defined for phosphines by Tolman,[35] a method to quantify the steric parameters of NHCs has been proposed by Nolan[31] who described NHCs as "fences" with "length" and "height".

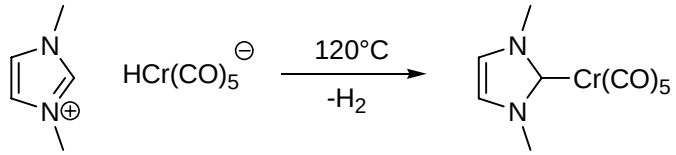
The structural differences for free NHCs and metal complexed NHCs are very small. In ^{13}C-NMR spectra, the signals for the free carbene carbon are usually shifted upfield by about 20-30 ppm upon complexation of the free NHC to a transition metal.

1.2.3 Complexation

Four synthetic methodologies have been most commonly applied in the literature for the preparation of NHC metal complexes: i) proton abstraction with bases prior to metalation, ii) *in situ* deprotonation of the imidazolium by basic metalates or basic counter-ions, iii) use of an external base in a one pot reaction with the metal, and iv) transmetallation via silver complexes.

NHCs are very strong σ donors and show dissociation energies higher than phosphines for a large range of metals (*vide supra*). Therefore, when their free form can be isolated, their complexation is achieved in high yield. It has been shown that free NHCs are able to cleave dimeric metallic species such as $[(\eta^4\text{-cod})RhCl]_2$[36] and exchange phosphine[25] or pyridine[37] ligands.

In his original work,[23] Öfele formed NHCs by *in situ* deprotonation of the corresponding imidazolium salts using the metal itself (Scheme 1.1). The basic metalate ion $[HCr(CO)_5]^-$ serves as base and ligand acceptors at the same time. One drawback of this method is the limited availability of the metal precursor.



Scheme 1.1 *In situ* deprotonation by a basic metalate ion

Basic counter-ions of the metal precursors can also act as deprotonating agents. For example, a convenient method to synthesise NHC-Pd(II) complexes is by mixing $Pd(OAc)_2$ with the corresponding imidazolium salt. In a similar way, μ-alkoxo complexes of (η^4-cod) rhodium(I) and iridium(I), formed in situ by adding μ-chloro bridged analogues to a solution of sodium alkoxide in the corresponding alcohol, will deprotonate an imidazolium salt and deliver the corresponding NHC complex.[26]

The use of an external base to generate NHCs in the presence of a metal precursor is also an efficient method. Potassium *tert*-butoxylate and sodium hydride in THF at room temperature can be used to co-ordinate NHCs to $Cr(CO)_6$ and to $W(CO)_6$ *in situ*.[38] A large variety of bases ranging from triethylamine,[39] lithium diisopropylamide[40] to phosphazene bases[41] have been successfully used over the past years.

Recently, a method for preparing NHC metal complex via silver complex has been developed by Wang.[42] Silver NHC complexes are readily prepared upon mixing the corresponding imidazolium salt with Ag_2O in CH_2Cl_2 at room temperature. Subsequent reaction with a chloro-metal precursor gives the desired NHC metal complex that can be easily separated from AgCl, the latter being insoluble in THF.

1.2.4 Abnormal binding modes for NHC ligands

In 2001, Crabtree discovered an unexpected binding mode of NHCs. Instead of having co-ordination at the C(2) position of the NHC, the metal was linked at C(4) or C(5) (Figure 1.8).[43] Since this publication, there have been an increasing number of reports of NHC with abnormal binding mode.[44-46]

Binding at C(2) Binding at C(4) or C(5)

Figure 1.8 C(2) and C(4) or C(5) binding mode of the NHCs.

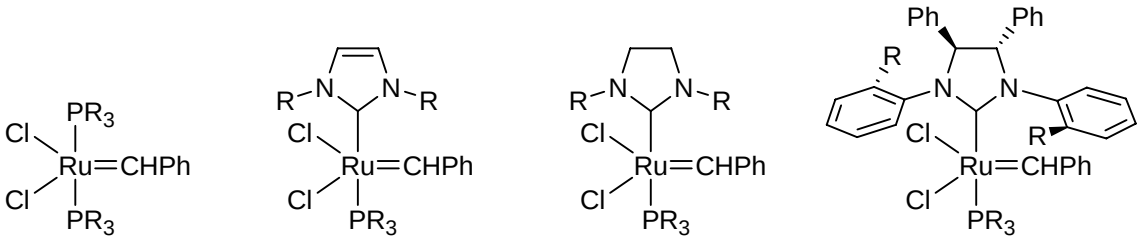
Non-classical carbene formation was initially observed by mixing pyridine-substituted imidazolium salts with $[IrH_5(PPh_3)_2]$ in refluxing C_6H_6. Since theoretical calculation predicts[47] that binding at the C(4) or C(5) position is less favoured, it was reasoned that steric effects of the bidentate pyridine-NHC around the metal centre controlled the reaction. However, the isolation of monodentate NHC complexes with a C(4) or C(5) binding mode proved that the chemistry involved is more complicated than previously thought. Abnormal co-ordination of NHCs is still intensively studied.

1.3 Catalysis involving NHCs

1.3.1 Ruthenium metathesis

Due to their σ-donor ability and their strong metal-carbon bond, NHC ligands have been applied as directing ligands in various catalytic transformations.[48] It is however in ruthenium-catalysed olefin metathesis type reactions that NHC ligands have proved their efficiency, giving access to unprecedented successful catalytic systems.

A breakthrough in catalytic metathesis reactions was achieved when NHC ligands were used to replace one of the phosphines of complex **17** (Figure 1.9). Herrmann showed that having one imidazolin-2-ylidene in place of a phosphine (**18**) favours the dissociative substitution of the phosphine ligand with an olefinic substrate, giving rise to a more active species.[29,49] Catalysts **18** showed excellent activities in the ring opening metathesis of 1,5-cyclooctadiene. In the same year, Grubbs introduced[50] a new generation of ring closing metathesis catalysts containing an even more basic NHC. Catalyst **19,** which contains an imidazolidin-2-ylidene ligand, showed outstanding activities combined with a large functional group tolerance. Moreover, the use of imidazolidin-2-ylidene allowed access to more chiral catalysts, by introduction of chirality at the C(4) and C(5) positions of the NHC. The application of complexes **20** in the desymmetrisation of triolefins yielded the ring closing metathesis products in high enantioselectivities.[51]



17 **18** **19** **20**

Figure 1.9 NHCs in ruthenium metathesis.

1.3.2 Asymmetric catalysis

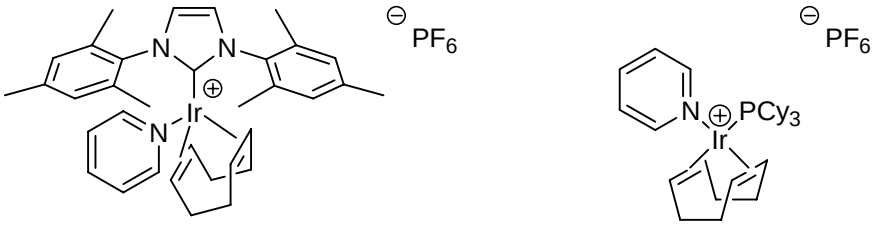
The first example of chiral carbenes used in asymmetric catalysis appeared in 1996/1997 with the pioneering work of Enders[52] and Herrmann.[53] Since then, the field has largely expanded and now there are many reports on the use of NHCs for asymmetric homogeneous catalysis.[54] Enders successfully applied the NHC and their derivatives in carbene catalysed asymmetric

nucleophilic acylation processes. High asymmetric induction in enantioselective benzoin condensation and enantioselective Stetter reactions were obtained by the use of simple chiral triazolium and thiazolium salt.

Chiral NHC ligands have been used in a large variety of metal asymmetric catalysed reactions. Applications to the following reactions were investigated: Rh-hydrosilylation of ketones,[53,55,56] olefin metathesis,[51,57] Pd-oxindole reaction,[58-60] Pd-allylic alkylation,[59] Rh(I)- and Ir(I)-transfer hydrogenation of ketones,[61] Cu-catalysed addition of diethylzinc to cyclohexenones,[62-64] Ni-hydroamination of acrylonitrile derivatives[65] and hydrogenation.

1.3.3 Hydrogenation

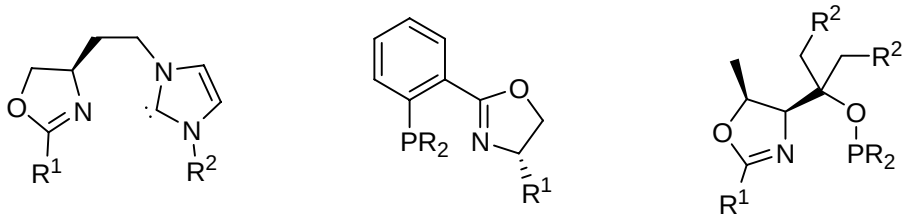
When our work was initiated in 2001, two reports on iridium-catalysed hydrogenation with NHC ligands were already published by Nolan and Burgess. Nolan initiated investigations into the field using achiral monodentate NHC iridium complex **21** for the hydrogenation of cyclohexene and 1-methylcyclohexene (Figure 1.10).[66] It was shown that catalyst **21** and Crabtree's catalyst **22** had comparable activity at room temperature. However, complex **21**, which was proven to be more robust than complex **22**, was more efficient at higher temperature.



21 **22**

Figure 1.10 Achiral monodentate NHC ligand and Crabtree's catalyst

A few months later, Burgess reported the first use of a bidentate oxazoline-NHC ligand **23** for asymmetric iridium-catalysed hydrogenation of unsubstituted alkenes (Figure 1.11).[67]

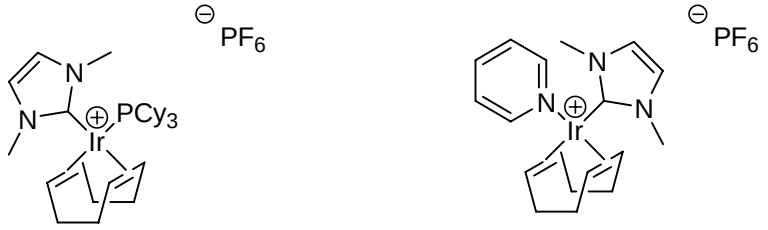


23 **24** **25**

Figure 1.11 Burgess's bidentate oxazoline-NHC ligands, PHOX ligands and its derivatives.

His remarkable system gave high enantioselectivities for a range of olefins approaching the best results obtained with the phosphino-oxazoline (PHOX) ligands **24** and its derivatives **25**.[68,69]

In 2002, Buriak showed that combining NHC with phosphine ligands led to efficient systems for the hydrogenation of simple olefins.[70] The comparison of complex **26** with its analogue **27,** for the hydrogenation of 1-methylcyclohexene and 2,3-dimethyl-2-butene, proved the superiority of catalyst **26** in term of activity (Figure 1.12). While complex **26** fully hydrogenated 2,3-dimethyl-2-butene in less than an hour at 1 bar H_2 and room temperature, complex **27** gave 19% conversion in four hours under the same conditions.



26 **27**

Figure 1.12 Achiral monodentate NHC phosphine and NHC pyridine iridium complexes.

Bolm took advantages of the planar chirality of paracyclophane to synthesise enantiopure bidentate ligands **28** and **29** (Figure 1.13).[71,72] In comparison with the Ir-PHOX complexes, both systems are less active and therefore require higher temperature and longer reaction time to go to completion. Although iridium catalysts containing NHC **29** gave higher asymmetric induction than iridium catalysts containing NHC **28**, the enantioselectivities were still low.

28 **29**

Figure 1.13 Bolm's paracyclophane based NHC bidentate ligands.

It is worth noticing that little work has been done on chiral NHC ligands for rhodium-catalysed asymmetric hydrogenation. To date, only two ligands have been reported (Figure 1.14). The first one, which was published in 2003 by Chung, is a bidentate NHC-phosphine ligand built on a ferrocene backbone (**30**).[73] Controlling the binding mode of ligand **30** to

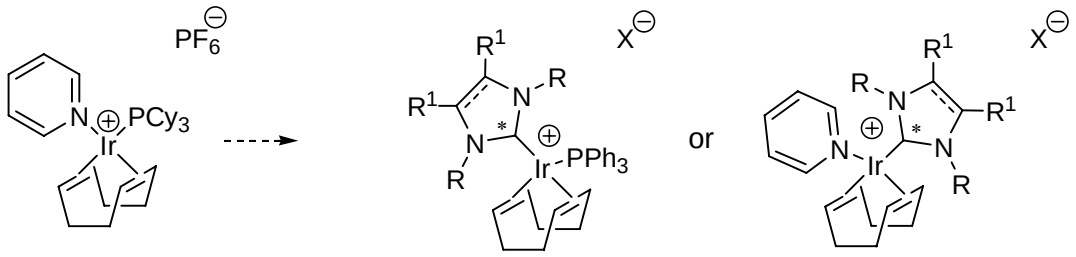
rhodium proved to be difficult. Nevertheless, the rhodium complexes studied showed very little activity and low enantioselectivities. The second report published by Helmchen also concerns a phosphine-NHC ligand (**31**), which possesses an chiral axis in addition to two centres of chirality.[74] Contrary to the previous system, Rh-catalyst containing NHC **31** performed very well, especially in terms of asymmetric induction. With Rh-catalysed asymmetric hydrogenation standard substrates such as dimethyl itaconate and *N*-acetyldehydroamino acid derivatives, almost perfect enantioselectivities were obtained after optimisation of reaction conditions.

30 **31**

Figure 1.14 Phosphine-NHC ligands tested in Rh-asymmetric hydrogenation.

1.4 Objectives of this work

The success encountered by monodentate achiral NHCs in iridium-catalysed hydrogenation of olefins[66,70] prompted us to start our work with the design of direct analogues of Crabtree's catalyst **32** and **33**. In these analogues, either the pyridine (**32**) or the phosphine (**33**) would be replaced by a monodentate *chiral* C_2-symmetric NHC (Figure 1.15).



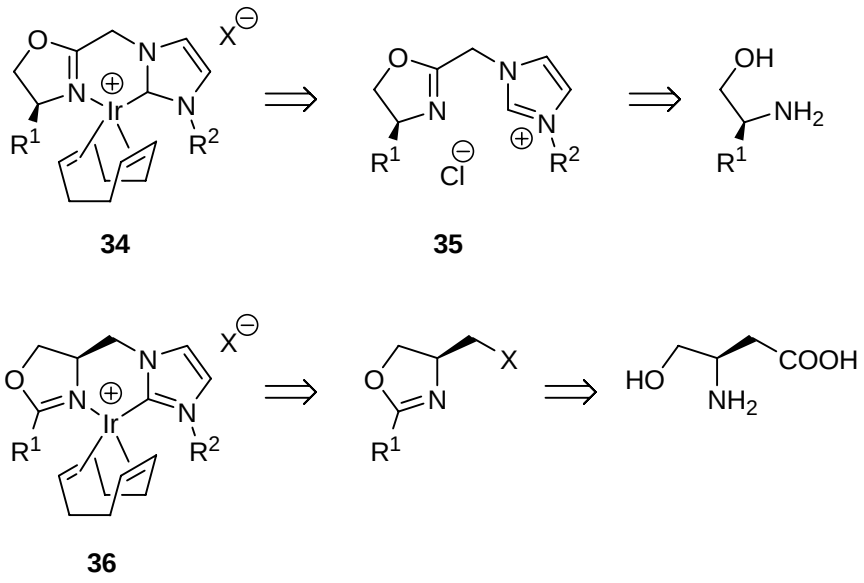
32 **33**

Figure 1.15 Derivation of Crabtree's analogues containing *chiral* C_2-symmetric NHC.

Another objective was to develop NHC chelating ligands, incorporating an oxazoline moiety. As a first investigation, a library of iridium complexes **34** could be synthesized starting from previously published imidazolium salt **35** (Figure 1.16).[75] One could expect these catalysts to

give higher asymmetric induction than their direct analogues derived from ligand **23**, since the six-membered chelating ring around the iridium centre would increase their conformational rigidity.

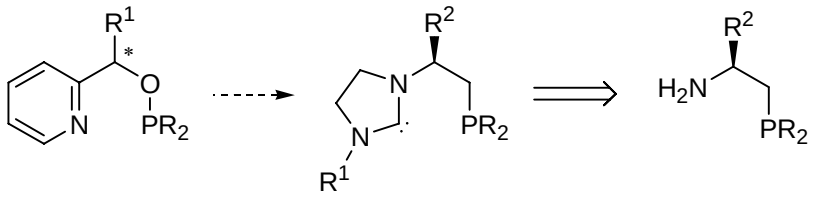
However, the R^1 substituent of catalysts **34** are synthetically restricted to those found in readily available amino-alcohols. We therefore planned to synthesise a second generation catalysts library **36,** where the R^1 substituent can be formed from derivatives of any carboxylic acid**,** thus allowing more variations in direct proximity to the iridium.



34 **35** **36**

Figure 1.16 NHC chelating ligands incorporating an oxazoline moiety.

Based on Buriak's and Bolm's reports,[70,72] which showed that iridium complexes bearing a phosphine and NHC are active in hydrogenation of unsubstituted olefins, we decided to synthesise new phosphine-NHC **38**. The synthesis of these ligands, which are closely related to the successful ligands **37** developed in our laboratory,[76] was devised starting from amino-phosphine **39** (Figure 1.17).



37 **38** **39**

Figure 1.17 Phosphine-NHC bidentate ligands.

During the course of this work, it has been shown that phosphinite containing ligands are almost always superior to their phosphine analogues in terms of enantioselectivity. Therefore, it was decided to devise a short convenient synthesis of phosphinite-NHC ligands starting from chiral epoxides (Figure 1.18).

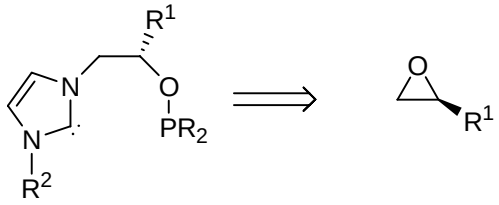


Figure 1.18 Phosphinite-NHC ligands synthesised from chiral epoxides.

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Chapter 2

Analogues of Crabtree's catalyst bearing chiral C_2-symmetric NHC

2.1 Introduction

In his pioneering work, Crabtree showed that iridium complex **40** was able to hydrogenate normally unreactive tri- and tetrasubstituted alkenes, lacking a coordinating group (Figure 2.1).[1-3] At that time, the enantioselective hydrogenation of prochiral functionalised alkenes, using chiral rhodium-phosphine complexes as catalysts, was well established: high activity and asymmetric induction were already observed in the case of aromatic dehydroamino acids.[4] In rhodium-catalysed hydrogenation, the functionality on the olefin is crucial for high enantiomeric excess since it becomes an additional coordination site for the metal and hold the substrate in a defined position leading to high stereoselectivity. In contrast to the latter, development of enantioselective catalysts for the hydrogenation of unfunctionalised olefins is difficult, since stereodifferentiation of the prochiral faces must be achieved, mainly via non-bonding, sterically-based interactions. A major breakthrough was achieved in the field when Pfaltz showed that good turnover numbers (TON) and high enantioselectivities were obtained for the hydrogenation of several imines and unfunctionalised alkenes using chiral bidentate phosphinooxazoline-iridium complexes **41**.[5,6]

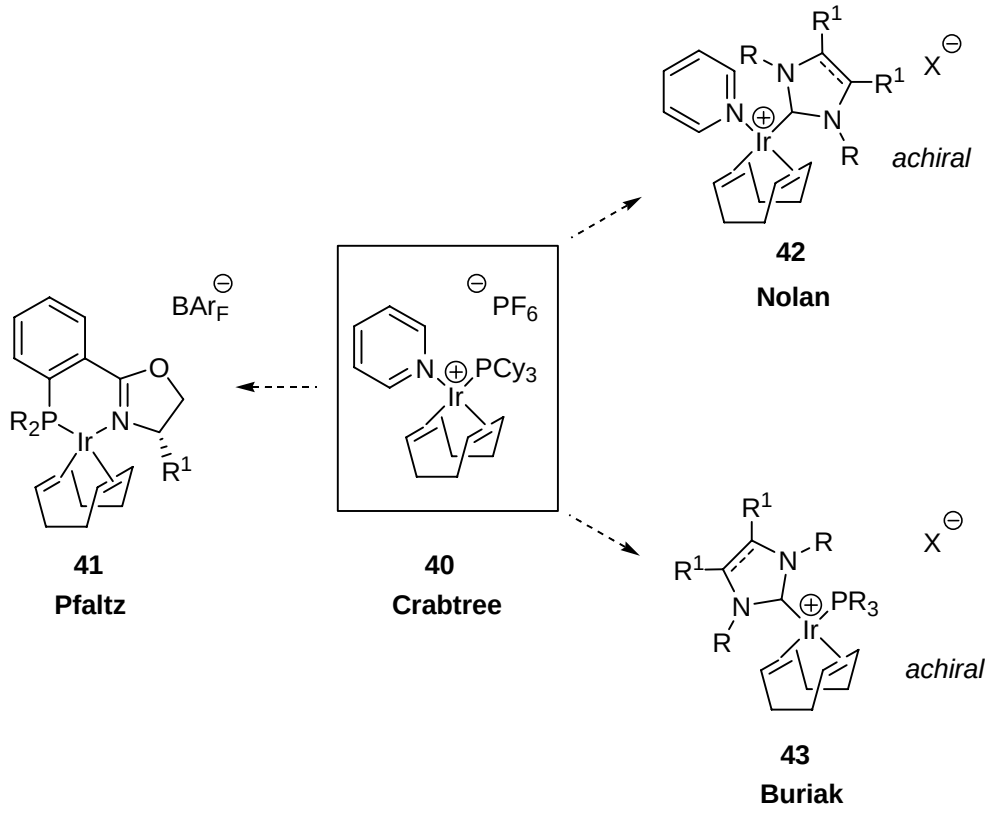


Figure 2.1 Crabtree's catalyst **40** and its derivatives **41**-**43**.

As discussed in the introduction chapter, it was recently shown that cationic achiral analogues of Crabtree's catalyst **42** and **43**, where the pyridine or the phosphine were replaced by NHCs, are active catalysts for hydrogenation of simple olefins such as methyl-cyclohexene (Figure 2.1).[7,8]

Based on these reports, we were interested in synthesising iridium complexes bearing one *chiral* C_2-symmetric NHC in combination with a phosphine or a pyridine unit and to test them in the enantioselective hydrogenation of unfunctionalised olefins.

In this project, two major issues were anticipated: i) activity of Crabtree's catalyst analogues with tri-substituted olefins and ii) asymmetric induction of chiral monodentate NHCs compared to bidentate ligands such as phosphinooxazolines **41**.

Crabtree's catalyst is known to be very effective in the hydrogenation of simple olefins. Although high TOFs (up to 8000 h^{-1}) are obtained for terminal and vicinal disubstituted olefins, catalyst deactivation prevents full hydrogenation of tri- and tetrasubstituted alkenes.[3] With their ability to bind metals strongly, NHCs are expected to give rise to robust catalysts (see chapter 1). We thought therefore that analogues of Crabtree's catalyst bearing C_2-symmetric NHCs would be less prone to catalyst deactivation and would allow the use of harsher reaction conditions.

Up to now, the best catalytic systems for iridium-catalysed hydrogenation are based on bidentate ligands such as **41**. One generally assumes that bidentate ligands lead to more effective chiral induction due to the rigidity they impose to the catalyst.[9] However, in some examples, monodentate ligands proved to be as enantioselective as the best bidentate ligands. Recently, Feringa and Reetz showed that monodentate phosphoramidites and phosphites give almost perfect asymmetric induction in rhodium-catalysed hydrogenation of dehydroamino acids (Figure 2.2).[10,11]

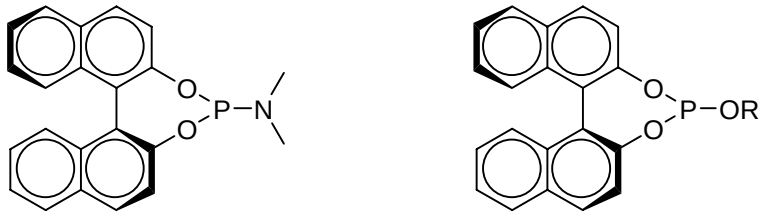
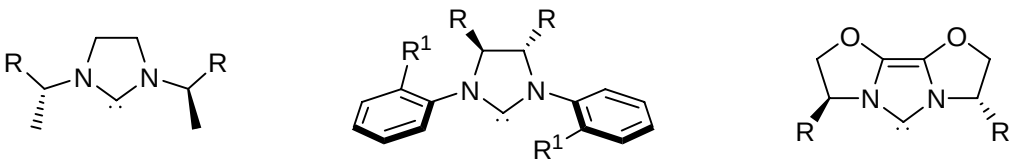


Figure 2.2 Monodentate phosphoramidites and phosphites used in enantioselective rhodium-catalysed hydrogenation.

Three different class of *chiral* C_2-symmetric NHC were chosen for this project (Figure 2.3).



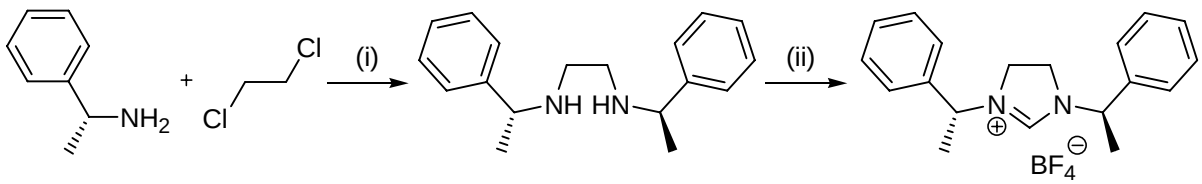
44 **45** **46**

Figure 2.3 The three different class of NHCs used.

In the first structure (**44**), chirality is incorporated in the *N*-substituents of the NHCs. The chirality of the second class of NHCs (**45**), which was developed by Grubbs,[12] is located at the C(4) and C(5) positions of the NHCs. For these NHCs, steric repulsions between the backbone R groups and the *o*-aryl R^1 groups are believed to stabilise an *anti*-conformation of the *N*-substituents, thus allowing efficient transmission of the chiral information to the active site of the catalyst. The third class of NHCs (**46**) developed by Glorius is derived from bioxazoline ligands.[13] With the *N*-substituents linked to the C(4) and C(5) positions of the backbone, these NHCs are the most rigid of the series.

2.2 Synthesis of imidazolium salts

Four different imidazolium salts were synthesised according to literature procedures. Imidazolium salt **49** was synthesised in two steps starting from commercially available chiral amine **47** (Scheme 2.1). Condensation of chiral amine **47** with 1,2-dichlorethane followed by vacuum distillation yielded secondary amine **48** in good yield.[14] Imidazolium salt **49** was obtained in high yield after ring closure using triethylorthoformate and ammonium tetrafluoroborate salt.

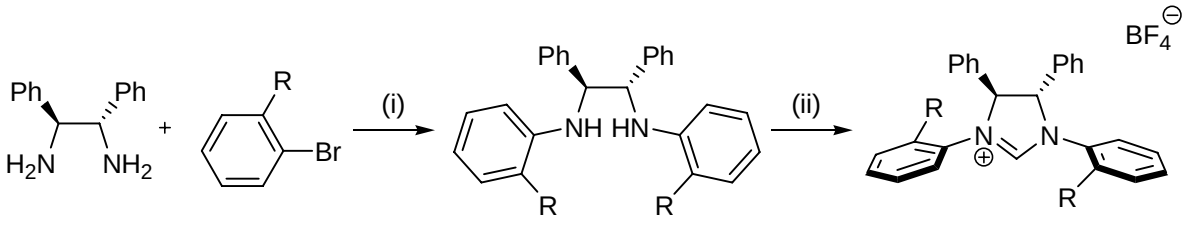


(*R*)-**47** (*R*,*R*)-**48** (*R*,*R*)-**49**

Reagents and conditions: (i) neat, 100°C, 16h, (74%); **(ii)** $HC(OEt)_3$ excess, NH_4BF_4, neat, 120°C, 14h, (95%).

Scheme 2.1 Synthesis of imidazolium salt **49**.

Imidazolium salts **53a** and **53b** were prepared according Grubbs' procedure (Scheme 2.2). Chiral diamine **50**, which was synthesised in five steps,[15] underwent Buchwald-Hartwig coupling reaction with bromoaryl **51a** and **51b** to yield diamine **52a** and **52b**. Ring closure with triethylorthoformate and tetrafluoroborate salt gave the desired imidazolium salts **53a** and **53b** in high yield.

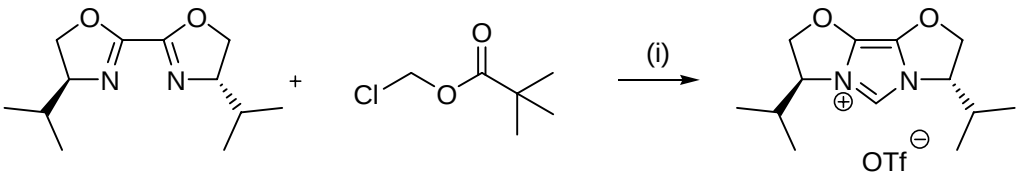


(*S*,*S*)-**50** | **51a** R = Me, **51b** R = *i*Pr | (*S*,*S*)-**52a** R = Me (82%), (*S*,*S*)-**52b** R = *i*Pr (88%) | (*S*,*S*)-**53a** R = Me (99%), (*S*,*S*)-**53b** R = *i*Pr (97%)

Reagents and conditions: (i) $Pd(OAc)_2$ (5 mol %), (±)-BINAP (10 mol %), NaO^tBu (3 eq.), toluene, reflux, 14h; **(ii)** $HC(OEt)_3$ excess, NH_4BF_4, neat, 120°C, 14h.

Scheme 2.2 Synthesis of imidazolium salts **53a** and **53b**.

Imidazolium salt **55** was also included in this project as part of a collaboration with Frank Glorius. Its synthesis was achieved in one step starting from bioxazoline ligand **54** via cyclisation using chloromethylpivalate and silver triflate (Scheme 2.3).[13]



(*S*,*S*)-**54** (*S*,*S*)-**55**

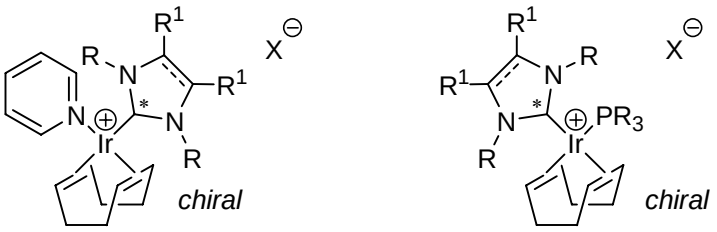
Reagents and conditions: (i) AgOTf, CH_2Cl_2, 40°C, 24h, (80%).

Scheme 2.3 Synthesis of imidazolium salt **55**.

2.3 Preparation of the iridium complexes

As already discussed in the introduction chapter, Crabtree's analogues, in which NHCs are combined with phosphines, are slightly more efficient in the hydrogenation of simple olefin than catalysts bearing NHCs and a pyridine unit. Since the difference in activity between the

two types of catalyst is not pronounced, we decided to synthesise two families of Crabtree's catalyst analogues **56** and **57** with pyridine and phosphine as co-ligand (Figure 2.4).



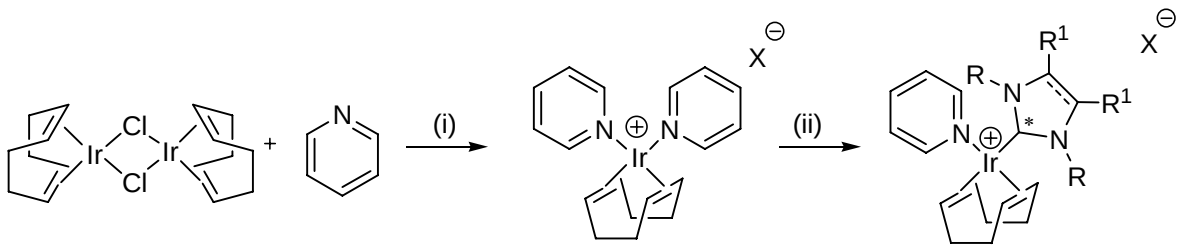
56 **57**

Figure 2.4 The two families of Crabtree's analogues **56** and **57**.

2.3.1 Analogues of Crabtree's catalyst bearing pyridine as co-ligand

Crabtree's analogues **56a** and **56b** containing two different counter-ions were synthesised, since the counter-ion of the Ir-PHOX catalysts has been shown to strongly influence the kinetic profile of asymmetric hydrogenation.[17,18] Previous work showed that reaction rates of Ir-PHOX catalysts were much higher with BAr_F^- counter-ion than with PF_6^- counter-ion.

Enantiopure complexes **56a** and **56b**, were synthesised by ligand exchange of one pyridine unit of iridium precursors **58a** and **58b** (Scheme 2.4).



58a X = BAr_F^- (97%) **56a** X = BAr_F^- (31-41%)
58b X = PF_6^- (95%) **56b** X = PF_6^- (52-86%)

BAr_F^- = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

Reagents and conditions: (i) $NaBAr_F$, CH_2Cl_2, RT, 8h for **58a**; NH_4PF_6, acetone/water (1:1), RT, 8h for **58b (ii)** imidazolium salt, BEMP, toluene, RT, 8h.

Scheme 2.4 Iridium precursors for NHC-pyridine iridium-complexes.

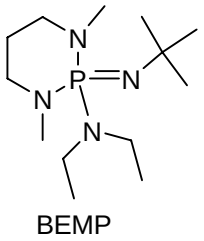
Iridium precursor **58a** was prepared according to a literature procedure.[16] Slight modifications of the procedure allowed synthesis of **58b**.

In order to replace one of the pyridine units of complexes **58a** and **58b** by NHCs, imidazolium salts must be deprotonated either before complexation or *in situ*. Since isolation of the free carbene from imidazolium salts **49**, **53a**, **53b** and **55** proved to be difficult, deprotonation of the imidazolium salts in presence of the metal precursor **56a** was chosen. A careful screen of the bases and reaction conditions was undertaken with imidazolium salt **53a** (Table 2.1). The purity of the products was confirmed by FAB-MS and ^{1}H-NMR.

entry	solvent	base	NHC/metal ratio	reaction condition	analyses
1	THF	NaH (in oil)	1:1	RT	s. m..
2	NH_3/THF (10/1)	NaH (in oil)	1:1	-78°C→RT	s.m. and prod.
3	THF	*n*BuLi	1:1	-78°C→RT	s.m. and prod.
4	THF	*n*BuLi	2:1	-78°C→RT	s.m. and prod.
5	THF	NaO^{t}Bu	1:1	RT	s.m. and prod.
6	Toluene	BEMP	1:1	RT	prod.

Table 2.1 Base screen for *in situ* generation of NHCs.

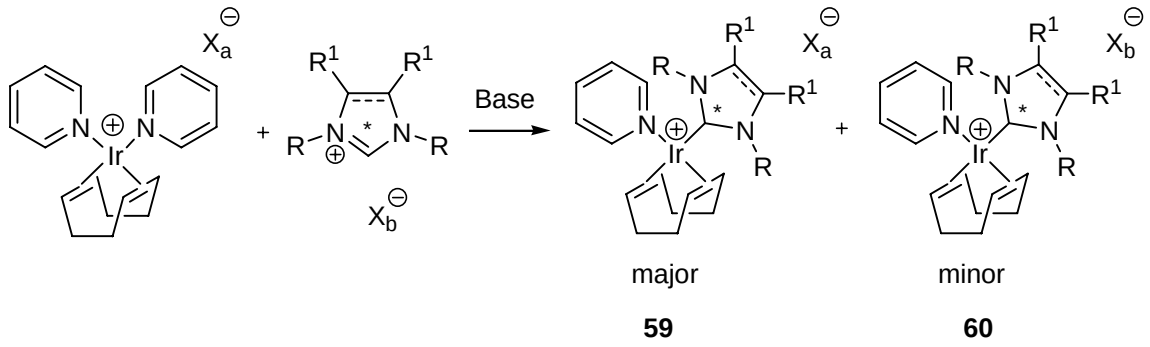
The choice of the base appeared to be crucial. None of the anionic bases generally used for *in situ* deprotonation of imidazolium salts were satisfactory (Table 2.1, Entry 1 to 5). The reactions failed to go to completion, even when using strong base as *n*Buli. The lack of reactivity of NaH, *n*BuLi and NaO^{t}Bu was attributed to their ability to react with the metal precursor instead of deprotonating the salt. Finally, non-anionic phosphazene base BEMP (Figure 2.5), which is 2000 times more basic and also much more sterically hindered than DBU,[19] proved to be suitable for *in situ* deprotonation of imidazolium salt **53a** (Table 2.1, Entry 6).



BEMP

Figure 2.5 Non anionic phosphazene BEMP base.

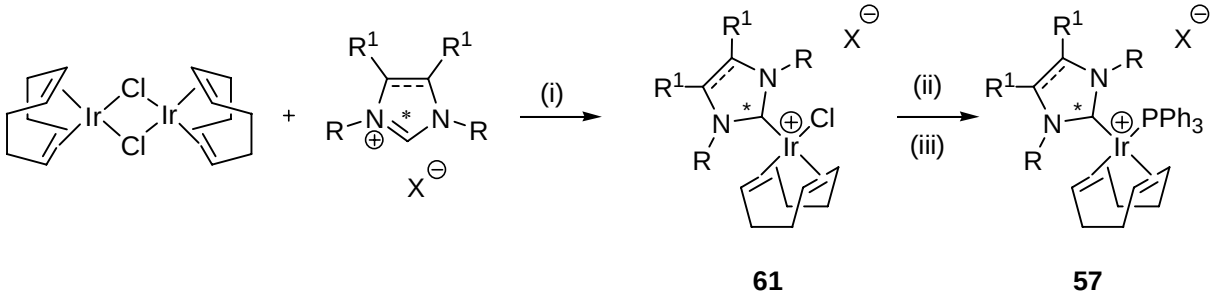
One drawback of *in situ* deprotonation of imidazolium salts is counter-ion scrambling (Scheme 2.5). Since two salts with different counter-ions are mixed in the reaction, the desired complex is likely to bear different anions. However, the minor undesired complex **60** was easily separated by chromatography on silica gel in every case.



Scheme 2.5 Counter-ion scrambling during synthesis of NHC-pyridine iridium complexes.

2.3.2 Analogues of Crabtree's catalyst bearing phosphine as co-ligand

Complexes **57**, in which the pyridine is replaced by a chiral NHC, were synthesised in two steps (Scheme 2.6). Starting from $[(\eta^4\text{-cod})IrCl]_2$, complexes **61** were prepared by *in situ* deprotonation of the imidazolium salts using BEMP. Abstraction of the chloride counter-ion from complexes **61** followed by addition of the triphenylphosphine gave the desired complexes **57** in good yield.



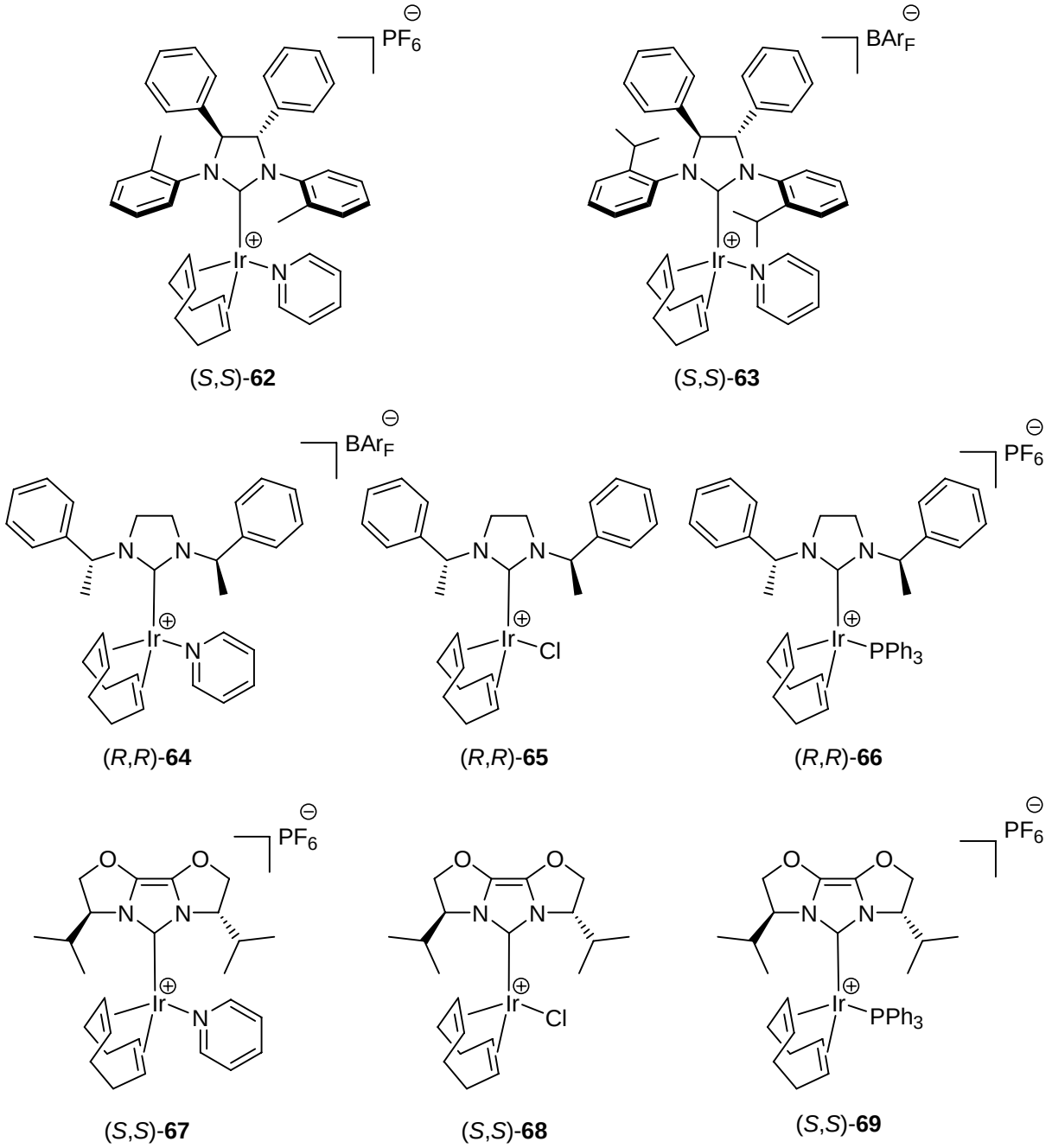
Reagents and conditions: (i) BEMP, CH_2Cl_2, RT, 2h; **(ii)** $AgPF_6$, CH_2Cl_2 / THF (1:1), RT, 15 min. **(iii)** PPh_3, THF, RT, 1h, (50-72 % overall yield).

Scheme 2.6 General procedure for the synthesis of NHC-phosphine iridium complexes **57**.

This procedure allows easy variation of the phosphine, since it is introduced in the last step of the synthesis. In the studies of monodentate achiral NHC phosphine iridium complexes for hydrogenation, Buriak combined a range of phosphines with 1,3-dimethylimidazolin-2-

ylidene.[8] Triphenylphosphine appeared to be the phosphine of choice and was therefore selected for our project.

An overview of all the complexes synthesised by the two methods described above is depicted in Figure 2.6. Four complexes **62**, **63**, **64** and **67** bear a pyridine unit as co-ligand. In this family, complexes **62** and **63** differ by their *ortho*-substituents on the aryl ring and their counter-ions (PF_6^- and BAr_F^-). Two complexes **66** and **69** have triphenylphosphine as co-ligand. They were both prepared with the PF_6^- counter-ion, which allowed efficient purification by crystallisation.



(*S*,*S*)-**62** (*S*,*S*)-**63**

(*R*,*R*)-**64** (*R*,*R*)-**65** (*R*,*R*)-**66**

(*S*,*S*)-**67** (*S*,*S*)-**68** (*S*,*S*)-**69**

Figure 2.6 Analogues of Crabtree's catalyst bearing chiral C_2-symmetric NHC.

2.4 Structural analysis of the iridium complexes

All complexes were characterised by standard 2D NMR analysis. Complexation of the C_2-symmetric imidazolium salts lowers the ligand symmetry from C_2 for the imidazolium salts to C_1 for the complexes. As a result, splitting of all the signals, except the NCN signal, is observed in the ^{1}H-NMR and ^{13}C-NMR spectra of the complexes. Complexation was monitored by the shift of the ^{13}C-NMR NCN signals from $\delta = 155(\pm 2)$ ppm for imidazolium salts **49**, **53a** and **53b** to $\delta = 202(\pm 2)$ ppm for the corresponding complexes. For NHC **46**, which has an unsaturated bond between C(4) and C(5), the ^{13}C-NMR NCN chemical shift is displaced from 116 ppm for imidazolium salt **55** to 155(±3) for complexes **67**-**69**.

Dynamic behaviour at room temperature was observed by NMR for complexes **62** and **63**. Complex **62** has two conformers in solution with a 100:7 ratio. NOESY experiments proved that the two conformers interchange at room temperature. In contrast to complex **62**, complex **63** has a complicated ^{1}H-NMR spectrum, thus making structural assignment difficult. At least, two interchangeable conformers are present at room temperature. The geometrical arrangement of the different conformers could not be established; neither for complex **62** nor complex **63**. The probable origin of the conformers is the position of the *ortho*-substituents, which can be orientated *anti* or *syn* relative to the phenyl substituents of the imidazole.

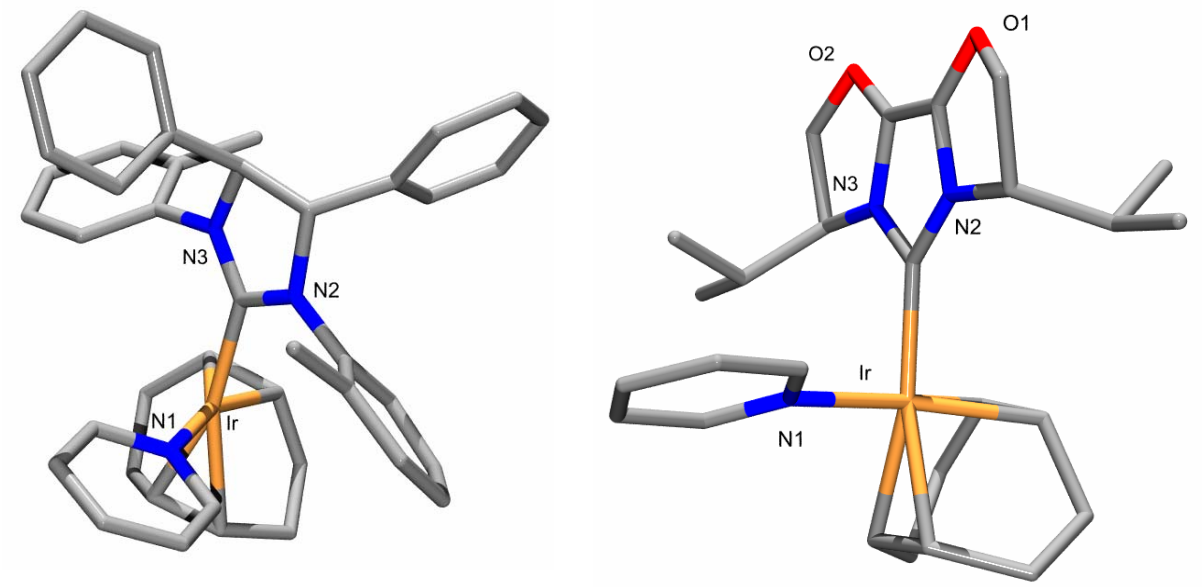


Figure 2.7 Crystal structures of (*S*,*S*)-**62** (left) and (*S*,*S*)-**67** (right). Counter-ion omitted for clarity.

Single crystals suitable for X-ray diffraction studies were obtained for complexes **62**, **65** and complex **67**. Unfortunately, the data for both complexes **62** and **67** were impossible to refine

satisfactorily. Despite acceptable R-values (6.4% for complex **62** and 6.9% for complex **67**), the structures can only be used to show the connectivity and the coordination geometry of the complexes (Figure 2.7).

As expected, the *N*-substituents of complex **62** are in an *anti-anti* arrangement relative to the phenyls of the imidazole ring. The X-ray structure analysis proves that in the solid state, the chiral information at the C(4) and C(5) positions of the imidazole is well transmitted to the active site of the catalyst. The crystal structure of complex **67** emphasises the rigidity of the NHC ligand, with the two isopropyl substituents pointing towards the iridium.

X-ray data of complex **65** were solved without any problems (Figure 2.8). In the same way as in the previous crystal structures, the iridium atom lies in an almost square planar arrangement, with the cyclooctadiene double bonds perpendicular to the plane of co-ordination. Although complex **65** is only the precursor of catalyst **66**, its crystal structure gives us an insight into the geometry adopted by the ligand for catalysts **64** and **66**. In the solid state, a C_2-symmetric arrangement of the NHC is the most stable structure. The methyl and phenyl substituents are pointing away from the iridium atom, leaving an empty cavity around the reaction centre. Therefore, despite the fact that the chirality centres are in proximity to the iridium, asymmetric induction of catalysts **64** and **66** is expected to be less efficient than for the other catalysts.

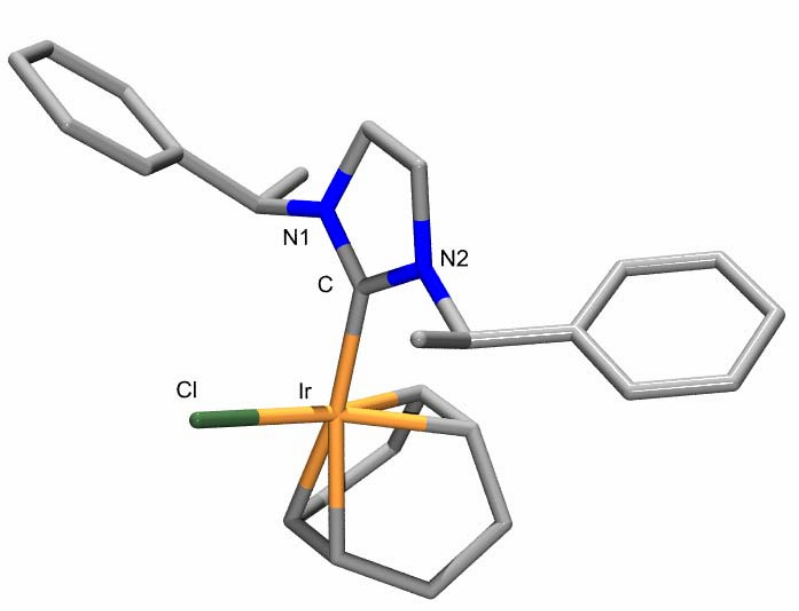
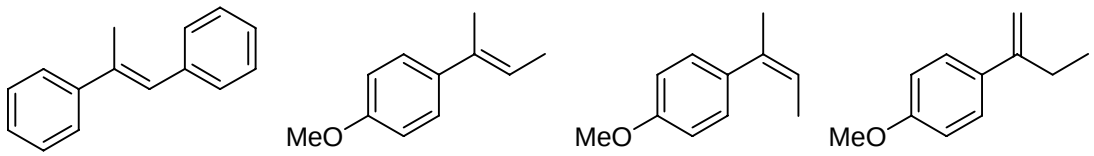


Figure 2.8 Crystal structures of (*R*,*R*)-**65**. Counter-ion and disorder of the N_1-phenyl ring omitted for clarity.

2.5 Hydrogenation

Analogues of Crabtree's catalyst **62-69** bearing C_2-symmetric chiral NHCs were tested in the asymmetric hydrogenation of a range of unfunctionalised olefins **70-73** (Figure 2.9). These substrates were chosen as they are difficult to hydrogenate with high enantiocontrol.



70 **71** **72** **73**

Figure 2.9 Substrates used for the screen of catalysts.

Since the activity of monodentate iridium catalysts with substrates **70-73** is not documented in the literature, a screen was undertaken with Crabtree's catalyst (Table 2.2) and with Nolan's achiral monodentate NHC-pyridine-iridium complex **74** (Table 2.3).

The performance of Crabtree's catalyst **40** with substrates **70-73** was tested using conditions generally applied for Ir-PHOX **41** and its derivatives (0.1 mmol substrate, 1 mol% catalyst, 50 bar H_2, 0.5 ml CH_2Cl_2, RT, 2h).[20] Trisubstituted alkenes (Table 2.2, Entry 1-3) showed very low conversion especially with *trans*-α-methylstilbene **70** (Table 2.2, Entry 1). Disubstituted olefin **73** performed reasonably well with 90% conversion.

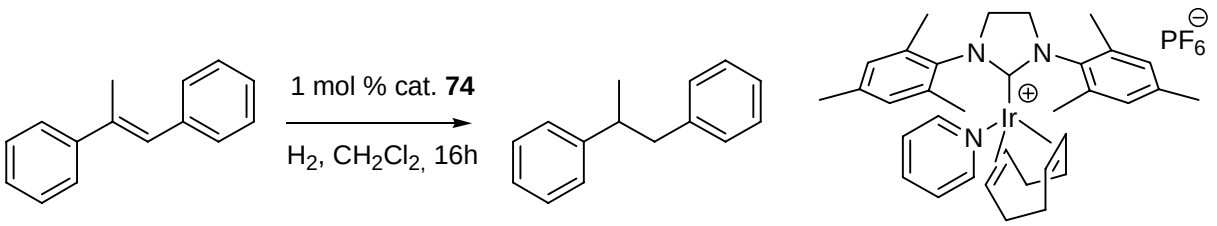
entry	substrate	H_2 pression (bar)	temperature (°C)	time (h)	conversion (%)
1	**70**	50	25	2	8
2	**71**	50	25	2	12
3	**72**	50	25	2	30
4	**73**	50	25	2	90

Table 2.2 Hydrogenation of substrates **70-73** using Crabtree's catalyst **40**.

In order to define the reaction conditions and achieve full conversion for *trans*-α-methylstilbene with monodentate NHC iridium complexes, temperature and pressure screen was performed with Nolan's achiral NHC-pyridine-iridium complex **74** (Table 2.3).

Despite a reaction time of 16 hours, almost no conversion was observed at 50 bar H_2 and room temperature (Table 2.3, Entry 1). Increasing the hydrogen pressure to 100 bar did not

improve efficiency of the catalytic system (Table 2.3, Entry 2). However, the activity of catalyst **74** was found to increase with temperature, and full conversion of *trans*-α-methylstilbene was obtained at 100°C (Table 2.3, Entry 3 and 4).



74

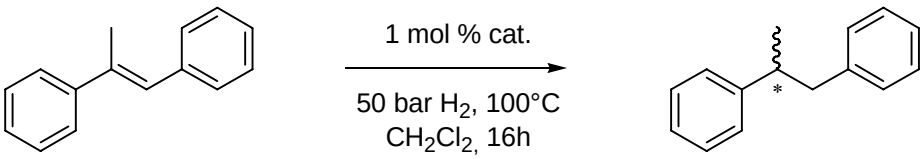
entry	H_2 pression (bar)	temperature (°C)	time (h)	conversion (%)
1	50	25	16	1
2	100	25	16	1
3	50	60	16	18
4	50	100	16	>99

Table 2.3 Hydrogenation of *trans*-α-methylstilbene with Nolan's catalyst **74**.

Analogues of Crabtree's catalyst bearing a C_2-symmetrical NHC **62-69** were tested for enantioselective hydrogenation of *trans*-α-methylstilbene under the conditions established in the preceding screen: 0.1 mmol substrate, 1 mol% catalyst, 50 bar H_2, 0.5 ml CH_2Cl_2, 100°C, 16h.

Only catalysts **63**, **64** and **67** gave full conversion. Catalysts **62** and **63** (Table 2.4, Entry 1 and 2) were the only catalysts that induced enantioselectivity. These quite remarkable results gave good evidence that these catalysts resisted the strong conditions applied. For catalysts **64** and **67**, which showed full conversion without asymmetric induction, it is not clear if the active species in the hydrogenation is the real catalyst, or another achiral catalytic species formed after complex degradation (Table 2.4, Entry 3 and 4). A considerable counter-ion effect was observed for complexes **62** and **63** (Table 2.4, Entry 1 and 2). *Trans*-α-methylstilbene was fully hydrogenated using catalyst **62** bearing BAr_F^- counter-ion, whereas its analogue **63** only reached 36% ee. Moreover, the small difference in enantioselectivity between **62** and **63** indicates that the *ortho*-substituents of the aryl rings have almost no influence on the stereochemical outcome of the hydrogenation. Very low activities were

observed for complexes **66** and **69** which proved to be non-stereoselective (Table 2.4, Entry 5 and 6).



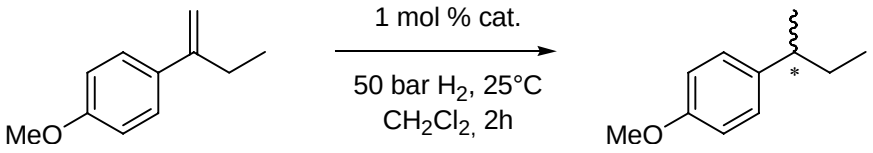
entry	catalyst	counter-ion	co-ligand	conversion[a] (%)	ee[b] (%)
1	**62**	PF_6^-	pyridine	36	34 (*S*)
2	**63**	BAr_F^-	pyridine	>99	30 (*S*)
3	**64**	BAr_F^-	pyridine	>99	0
4	**67**	PF_6^-	pyridine	>99	0
5	**66**	PF_6^-	PPh_3	7	0
6	**69**	PF_6^-	PPh_3	12	-

[a] Determined by GC. [b] Determined by HPLC.

Table 2.4 Hydrogenation of *trans*-α-methylstilbene with catalysts **62**-**69**.

The very low activities observed and strong reaction conditions required for the hydrogenation of *trans*-α-methylstilbene, prompted us to investigate hydrogenation of disubstituted olefin **73**. Disubstituted olefin **73** is known to be more easily hydrogenated than trisusbstituted olefins. Pfaltz showed that a strong hydrogen pressure dependence was observed for this substrate, which reacts with higher enantioselectivity at low pressure. [20] We therefore tested our catalysts with substrate **73** using two sets of condition: i) 50 bar H_2, RT, 2h (Table 2.5) and ii)1 bar H_2, RT, 2h (Table 2.6).

At 50 bar H_2, almost all catalysts were able to fully hydrogenate alkene **73**. However, the enantioselectivities measured are rather low. Catalysts bearing NHC type **45** showed almost no asymmetric induction (Table 2.5, Entry 1 and 2). The highest enantioselectivity (20% ee) was obtained with catalyst **66** (Table 2.5, Entry 5). The effect of triphenylphosphine or pyridine as co-ligand seems to be NHC dependent. While NHC of type **44** induces higher enantiomeric excess in combination with triphenylphosphine (Table 2.5, Entry 3 and 5), NHC type **46** is more enantioselective when combined with pyridine (Table 2.5, Entry 4 and 6).

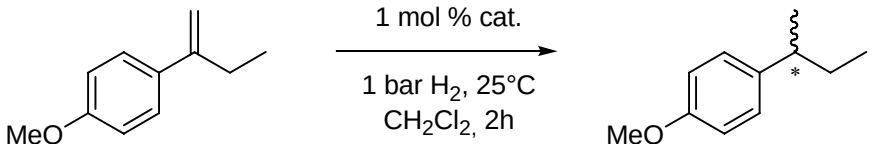


entry	catalyst	counter-ion	co-ligand	conversion[a] (%)	ee[b] (%)
1	**62**	PF_6^-	pyridine	>99	5 (*R*)
2	**63**	BAr_F^-	pyridine	>99	5 (*R*)
3	**64**	BAr_F^-	pyridine	>99	11 (*S*)
4	**67**	PF_6^-	pyridine	96	13 (*R*)
5	**66**	PF_6^-	PPh_3	>99	20 (*S*)
6	**69**	PF_6^-	PPh_3	>99	0

[a] Determined by GC. [b] Determined by HPLC.

Table 2.5 Hydrogenation of 2-(4-methoxyphenyl)-1-butene with catalysts **62-69** at 50 bar H_2.

At 1 bar H_2, all the catalysts were less active than at 50 bar H_2. The TONs were still acceptable, with the exception of **62** (Table 2.6, Entry 1), which required 3 mol% catalyst to achieve 30% conversion in 2 hours. As already observed during hydrogenation of *trans*-α-methylstilbene, catalysts **62** and **63** show a counter-ion effect. With BAr_F^- counter-ion the activity is higher than with PF_6^- (Table 2.6, Entry 1 and 2). No significant difference in activity was observed between NHC iridium catalysts bearing pyridine and those bearing triphenylphosphine. As expected, lowering the pressure to 1 bar H_2 had a positive effect on the asymmetric induction. The enantioselectivities measured at 1 bar H_2 were all largely superior to those measured at 50 bar H_2. Astonishingly, reduction of the pressure to 1 bar H_2 for catalyst **66** resulted in inversion of enantioselectivity (Table 2.6, Entry 5 and Table 2.6, Entry 5). As already observed for hydrogenation of *trans*-α-methylstilbene, changing the methyl *ortho*-substituent of catalyst **62** to an isopropyl substituent (catalyst **63**) did not lead to higher enanatioselectivities (Table 2.6, Entry 1 and 2). For catalysts bearing pyridine as co-ligand, the rigidity of the *N*-substituent of the imidazole seems to be an important factor for asymmetric induction: the more rigid the *N*-substituents (**64** < **63** < **67)**, the higher the enantioselectivities (Table 2.6, Entry 2-4). No improvement in activity was noted when triphenylphosphine was used instead of pyridine. As already observed at 50 bar H_2, the choice of triphenylphosphine or pyridine as co-ligand does not affect significantly the asymmetric induction (Table 2.6, Entry 3 versus 5 and Entry 4 versus 6).



entry	catalyst	counter-ion	co-ligand	conversion[a] (%)	ee[b] (%)
1	**62**	PF_6^-	pyridine	30[c]	21 (*R*)
2	**63**	BAr_F^-	pyridine	40	25 (*R*)
3	**64**	BAr_F^-	pyridine	61	14 (*S*)
4	**67**	PF_6^-	pyridine	88	44 (*R*)
5	**66**	PF_6^-	PPh_3	50	22 (*R*)
6	**69**	PF_6^-	PPh_3	72	35 (*R*)

[a] Determined by GC. [b] Determined by HPLC. [c] 3 mol % catalyst.

Table 2.6 Hydrogenation of 2-(4-methoxyphenyl)-1-butene with catalysts **62-69** at 1 bar H_2.

2.6 Conclusion

A family of six iridium complexes bearing monodentate NHC ligands, and pyridine or triphenylphosphine as co-ligand, were synthesised starting from readily available C_2-symmetric imidazolium salts.

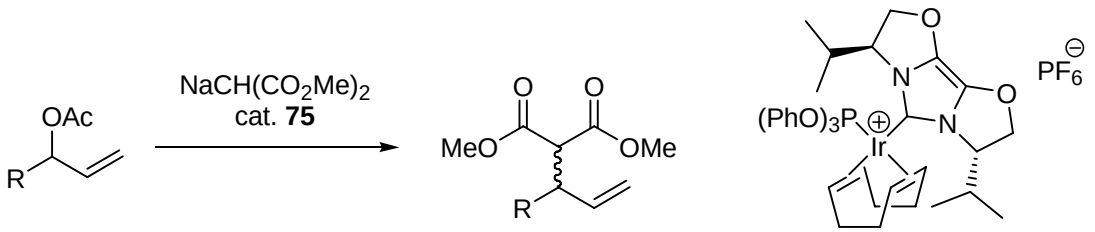
Full characterisation by standard 2D NMR techniques and X-ray diffraction studies were undertaken to investigate the dynamic behaviour and geometry of the NHC ligands. Complexes **62** and **63**, bearing NHC **45** developed by Grubbs, showed a dynamic behaviour as observed by NMR. X-ray data analysis strongly suggests that the geometry of the *ortho*-substituents of the *N*-aryl groups in solution is *anti-anti* relative to the phenyls of the imidazole.

In terms of both activity and enantioselectivity, analogues of Crabtree's catalyst bearing C_2-symmetric chiral NHC are not suitable for trisubstituted olefins. Full conversions were only obtained under harsh conditions (50 bar H_2, 100 °C, 16h). However, these experiments highlight the remarkable robustness of catalysts **62** and **63**, which gave enantiomeric excesses up to 34% ee.

With terminal olefin **73**, a reasonable activity was observed. Full conversions were obtained at 50 bar H_2, 25°C, 2h. The low asymmetric induction obtained at 50 bar H_2 was improved by lowering the pressure to 1 bar. At 1 bar H_2, the activities were still acceptable with low to

moderate enantiomeric excesses (up to 44% with complex **67**). The choice of pyridine or triphenylphosphine as co-ligand does not significantly affect the activity of the catalysts. In terms of asymmetric induction, no clear trend was observed.

Analogues of Crabtree's catalyst bearing a C_2-symmetrical NHC may find applications in other iridium-catalysed reactions. In particular, NHC ligands combined with triphenyl phosphite could give rise to interesting systems for iridium-catalysed allylic alkylation (Scheme 2.7).



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Scheme 2.7 Possible application of C_2-symmetric NHCs in combination with $P(OPh)_3$ for iridium-catalysed allylic alkylation.

It has been recently shown that iridium-phosphoramidite complexes prepared *in situ* can achieve enantioselectivities up to 86% ee.[21] By combining the strong σ-donor NHC with $P(OPh)_3$, the large electronic difference of the ligands should allow effective regiocontrol in the iridium-catalysed allylic alkylation of monosubstituted allylic substrates, thus leading to high enantioselectivities.

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Chapter 3

Oxazoline-imidazolin-2-ylidene ligands

3.1 Introduction

Chiral phosphino-oxazolines **A** (PHOX ligands) and related compounds such as **B** are highly versatile and efficient ligands for the enantioselective iridium-catalysed hydrogenation of imines and a wide range of functionalised and unfunctionalised olefins (Figure 3.1).[1-4] In order to improve the enantioselectivity and widen the application range, many variants of ligands **A** and **B** have been synthesised, giving rise to a large library of P,N-ligands.[5] In addition, a series of pyridyl-phosphinites **C** and related pyridine- and quinoline-derived ligands, which were devised to mimic the co-ordination sphere of Crabtree's catalyst ($[Ir(PCy_3)(pyridine)(cod)]PF_6$)[6] were developed in our group. These ligands also showed high asymmetric induction in iridium-catalysed hydrogenations.[7] Other groups as well have reported efficient P,N-ligands containing a pyridine or oxazole as co-ordinating units.[8,9]

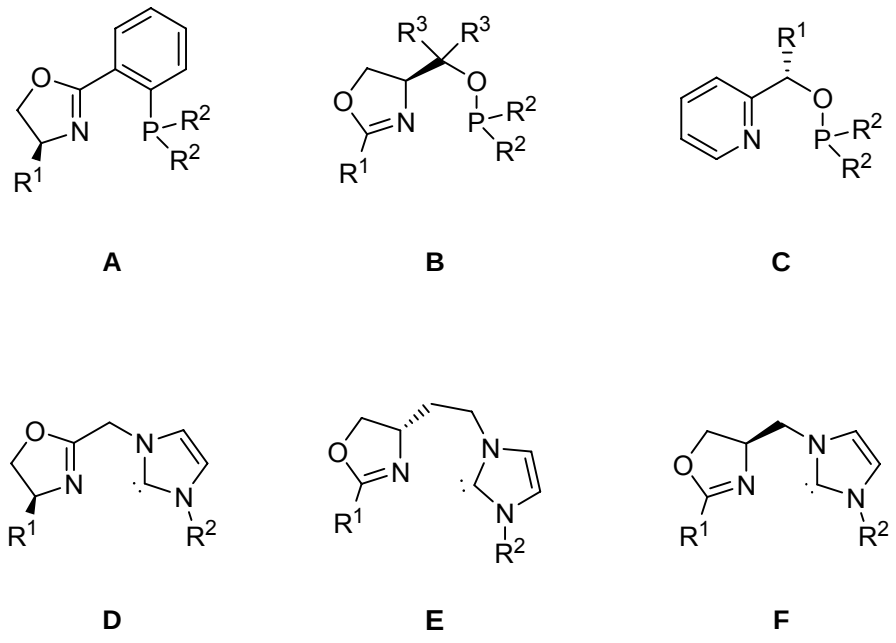


Figure 3.1 P,N-ligands for the enantioselective iridium-catalysed hydrogenation and their oxazoline-carbene analogues.

Recently, Burgess *et al.* synthesised chiral iridium complexes from ligands **E** containing a seven-membered chelate ring, in which phosphorus was replaced by a *N*-heterocyclic carbene (NHC).[10,11] Among the various derivatives tested, one particular structure **E1**, with R^1 = 1-adamantyl and R^2 = 2,6-diisopropylphenyl clearly gave the best enantioselectivities

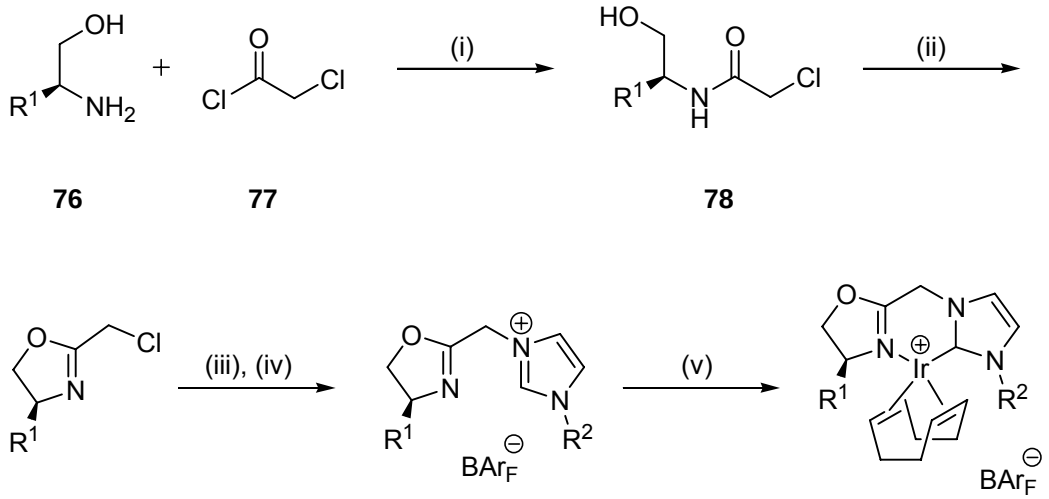
with 98% ee for *trans*-α-methylstilbene. Although high enantioselectivities were observed for a range of substrates with this ligand, the overall performance was still inferior to the most efficient P,N-ligands. Because the most efficient P,N-ligands for iridium-catalysed hydrogenation all form six-membered chelate rings, we became interested in evaluating NHC-oxazoline ligands, forming a six-membered chelate ring. (Oxazoline-imidazolin-2-ylidene ligands forming five-membered rings were developed and studied by Gade *et al.*[12,13])

Previously reported ligands **D** were thought to be good candidates for this study.[14] However, the R^1 group in ligands **D** is restricted to substituents found in readily available amino alcohols. In addition, in view of the good results obtained with ligands **B**, we devised a second generation of oxazoline-carbenes (structure **F**), in which the R^1 substituents are formed from derivatives of almost any carboxylic acid, thus giving more scope for diversity.

3.2 Synthesis of chiral imidazolium salts

The syntheses of imidazolium salts **80a**-**g** and **89a**-**p**, which are precursors of ligands **D** and **F** are summarised in Schemes 3.1 and 3.2. Imidazolium salts **80a**-**g** were synthesised using a divergent pathway, in which the imidazolium salt moiety is introduced in the last step, thus allowing easy variation of the imidazolin-2-ylidene substituents. This route differs from the previously published synthesis[14] that starts from an imidazole and introduces the oxazoline ring at the end. The key intermediates, chloromethyloxazolines **79**,[15] were prepared by condensation of chloroacetyl chloride **77** with (*S*)-*tert*-leucinol or (*S*)-valinol, followed by ring closure using Burgess reagent.[16,17] After purification by distillation, chloromethyloxazolines **79** were reacted with a range of imidazoles, which were either commercially available or prepared according to literature procedures.[18-20] The resulting imidazolium chlorides were treated with $NaBAr_F$ (BAr_F^- = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) to give the corresponding BAr_F^- salts **80a**-**g** in moderate to high yield.

The weakly co-ordinating BAr_F^- counter-ion was used for two reasons. Firstly, it allowed simple purification of imidazolium salts **80a**-**g** by standard chromatography on silica gel, which was not possible with the corresponding chloride salts. Secondly, the BAr_F^- anion is known to improve the performance of iridium complexes as hydrogenation catalysts compared to other weakly co-ordinating anions such as hexafluorophosphate, tetrafluoroborate or triflate.[21,22]

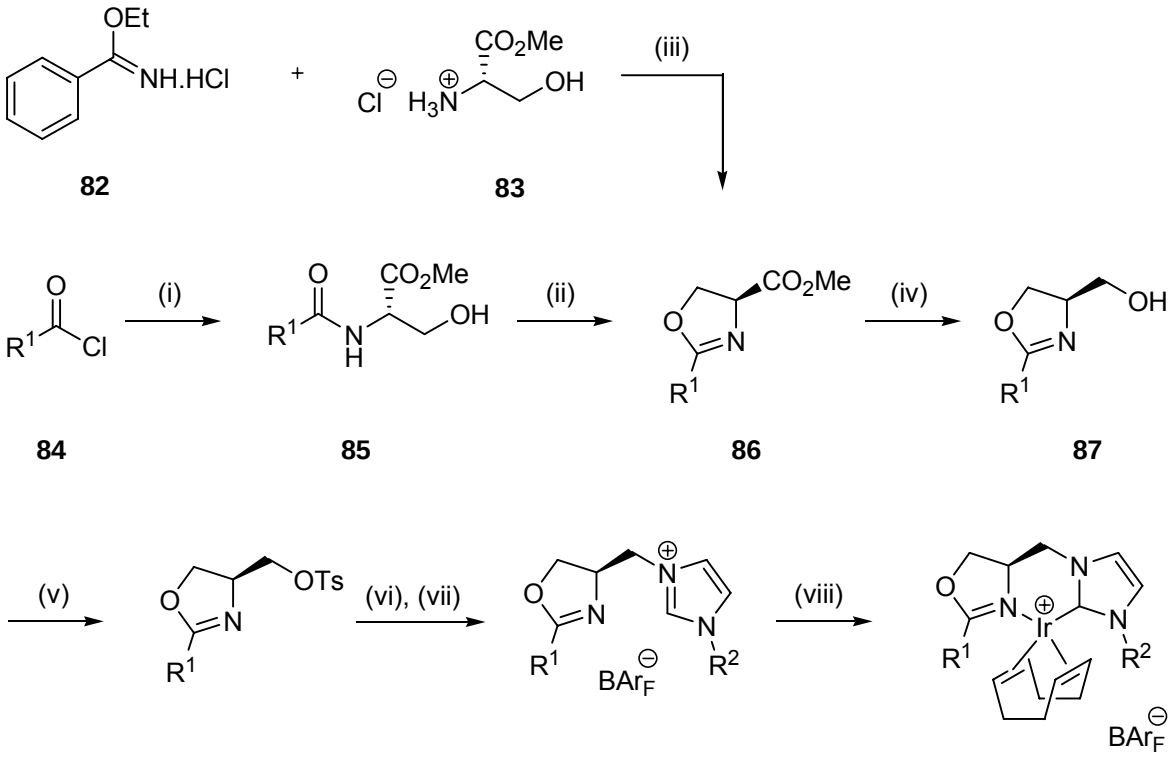


80a	R^1 = *t*Bu, R^2 = Me	**80e**	R^1 = *t*Bu, R^2 = Neopentyl
80b	R^1 = *i*Pr, R^2 = Me	**80f**	R^1 = *t*Bu, R^2 = Isobutyl
80c	R^1 = *t*Bu, R^2 = *i*Pr	**80g**	R^1 = *t*Bu, R^2 = *t*Bu
80d	R^1 = *t*Bu, R^2 = 2,4,6-$Me_3C_6H_2$		

Reagents and conditions: (i) NEt_3, CH_2Cl_2, RT, 10h, (83-89%); **(ii)** Burgess reagent, THF, reflux, 4h (50-66%); **(iii)** Imidazole, DMF, 80°C, 8h; **(iv)** $NaBAr_F$ (BAr_F^- = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), CH_2Cl_2, RT, 15 min, (58-78% over two steps); **(v)** $[(\eta^4\text{-cod})IrCl]_2$, NaO*t*Bu, THF, RT, 3h, (44-65%).

Scheme 3.1 Synthesis of iridium complexes **D**.

In the synthesis of ligands **F**, the imidazolium moiety was again introduced in the last step (Scheme 3.2). Oxazolines **86** were obtained by reacting (*S*)-serine methyl ester hydrochloride **83**, either with commercially available benzimidate hydrochloride **83**, or with acyl chlorides **84** followed by ring closure using Burgess reagent. Reduction of the ester group using DIBAL in THF gave oxazoline alcohols **87** in moderate to good yields. Tosylation and subsequent nucleophilic substitution with a range of imidazoles yielded the corresponding imidazolium tosylates, which were converted into BAr_F^- salts **89a-p** by anion exchange with $NaBAr_F$, followed by flash chromatography on silica gel. By this method, four different sets of ligands (R^1 = *tert*-butyl, adamantyl, 2,6-dimethylphenyl and phenyl) with various R^2 groups were prepared.



89a R^1 = *t*Bu, R^2 = Me
89b R^1 = *t*Bu, R^2 = *i*Pr
89c R^1 = *t*Bu, R^2 = 2,4,6-$Me_3C_6H_2$
89d R^1 = *t*Bu, R^2 = Neopentyl
89e R^1 = *t*Bu, R^2 = *t*Bu

89f R^1 = 1-Ad, R^2 = Me
89g R^1 = 1-Ad, R^2 = *i*Pr
89h R^1 = 1-Ad, R^2 = 2,4,6-$Me_3C_6H_2$
89i R^1 = 1-Ad, R^2 = Neopentyl
89j R^1 = 1-Ad, R^2 = *t*Bu

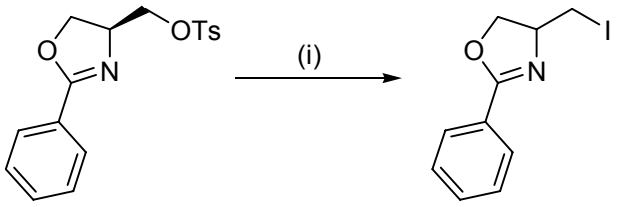
89k R^1 = 2,6-$Me_2C_6H_3$, R^2 = Me
89l R^1 = 2,6-$Me_2C_6H_3$, R^2 = *i*Pr
89m R^1 = 2,6-$Me_2C_6H_3$, R^2 = 2,4,6-$Me_3C_6H_2$
89n R^1 = 2,6-$Me_2C_6H_3$, R^2 = Neopentyl
89o R^1 = 2,6-$Me_2C_6H_3$, R^2 = *t*Bu

89p R^1 = Ph, R^2 = 2,4,6-$Me_3C_6H_2$

Reagents and conditions: (i) (*S*)-serine methyl ester hydrochloride, NEt_3, CH_2Cl_2, RT, 10h, (80-93%); **(ii)** Burgess reagent, THF, reflux, 4h (65-72%); **(iii)** 1,2-dichlorethane, reflux, 20h, (91%); **(iv)** DIBAL, THF, RT, 12h, (52-78%); **(v)** NEt_3, TsCl, CH_2Cl_2, RT, (50-83%); **(vi)** Imidazole, DMF, 80°C, 8h; **(vii)** $NaBAr_F$ (BAr_F^- = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), acetone, RT, 15 min (50-78% over two steps); **(viii)** $[(\eta^4\text{-cod})IrCl]_2$, NaO*t*Bu, THF, RT, 3h, (48-83%).

Scheme 3.2 Synthesis of iridium complexes **F**.

Iodide derivates **88bis,** synthesised from tosylate **88p** (Scheme 3.3), were also prepared in order to determine if iodide would be a better leaving group than tosylate for nucleophilic substitution by imidazoles. However, racemisation occurred during synthesis of iodides **88bis** and their reactivity with the imidazoles was not investigated.



88p **88bis**

Reagents and conditions: (i) NaI, acetone, 50°C, 16h, (94%).

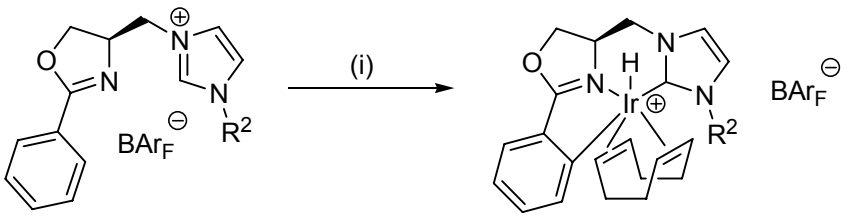
Scheme 3.3 Synthesis of iodide **88bis**.

3.3 Preparation of the iridium complexes

Cationic iridium(I) complexes **81a-f** and **90a-o** were synthesised in a one-step procedure, starting from the corresponding imidazolium salts **80a-g** and **89a-o** (Schemes 3.1 and 3.2). Deprotonation at the imidazolium ring[23,24] using sodium *tert*-butoxide in the presence of $[(\eta^4\text{-cod})IrCl]_2$ allowed simultaneous generation and complexation of the *N*-heterocyclic carbene.[25] The chloride anions were removed from the reaction mixture by precipitation of NaCl. The resulting yellow to orange crystalline BAr_F^- salts were purified by flash chromatography on silica gel.

Whereas complexation of imidazolium salts **80a-f** was successful, no complex formation was observed with imidazolium salt **80g**, even when more forcing conditions with a strong base such as *n*BuLi were applied. In this particular case, steric hindrance by the two *tert*-butyl substituents seems to prevent complexation of imidazolium salt **80g** to iridium. However, the analogous imidazolium salt **89e**, which also contains two *tert*-butyl groups, was metalated in respectable yield (59%).

Under the reaction conditions described above, complexation of imidazolium salt **89p** gave an unexpected product **90p** as a colorless powder in 84% yield (Scheme 3.3). Full characterisation, including single crystal X-ray diffraction analysis, allowed the assignment of structure **90p**. Apparently, complexation of ligand **89p** was accompanied by insertion of the Ir(I) centre into one of the *ortho* C-H bonds of the phenyl substituents at the oxazoline ring.



89p **90p**

Reagents and conditions: (i) i) $[(\eta^4\text{-cod})IrCl]_2$, NaO*t*Bu, THF, 3h, (84%).

Scheme 3.3 Synthesis of complex **90p**.

The presence of an Ir-bound hydride, resulting from C-H activation, was proved by the observation of a hydride signal at $\delta = -14.6$ ppm in the ^{1}H-NMR spectrum. The crystal structure of **90p** shows the iridium atom in a pseudo-octahedral co-ordination environment with the iridium atom lying within 0.02 Å in the best plane fitted through the carbene atom C(13), the phenyl C(1) atom and the midpoints of the cyclooctadiene double bonds (Figure 3.2). This geometry implies that the hydride is located *trans* to the oxazoline ring. Since complex **90p** proved to be catalytically unreactive in hydrogenation, no other complexes of this type were synthesised.

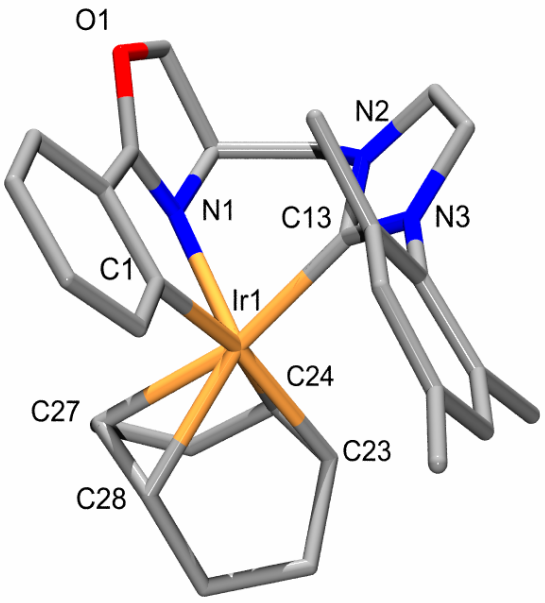


Figure 3.2 Structure of the cation of **90p**. Selected bond lengths (Å) and angles (°): Ir(1)-C(1) 2.029(4), Ir(1)-N(1) 2.159(3), Ir(1)-C(13) 2.054(4), Ir(1)-C(23) 2.281(4), Ir(1)-C(24) 2.300(4), Ir(1)-C(27) 2.226(4), Ir(1)-C(28) 2.248(4), C(23)-C(24) 1.380(7), C(27)-C(28) 1.373(7); N(2)-C(13)-N(3) 104.3(3), N(1)-Ir(1)-C(1) 78.27(15), C(13)-Ir(1)-N(1) 78.34(14).

3.4 Structural analysis of the iridium complexes

All ^{13}C and ^{1}H resonances of complexes **81a-f** and **90a-o** were assigned by standard 2D NMR techniques. In the ^{13}C-NMR spectra, a shift of the NCN signal from δ = 134(±3) ppm for the imidazolium salts to δ = 173(±4) ppm for the carbene complexes was observed upon NHC complexation.

Single crystals, suitable for X-ray analysis were obtained for complexes **81b** and **90q**, the latter being an analogue of complex **90b** with PF_6^- instead of BAr_F^- as counter-ion (Figures 3.3 and 3.4). Synthesis of **90q** was achieved by reacting $[(\eta^4\text{-cod})IrCl]_2$ and NaO*t*Bu in THF at room temperature with the corresponding imidazolium salt bearing a chloride counter-ion, followed by addition of $TlPF_6$ in CH_2Cl_2 at room temperature.

In both crystal structures, the iridium atom adopts a nearly square planar co-ordination geometry with the cod double bonds perpendicular to the co-ordination planes. The bond angles observed at the carbene centres, N(2)-C(14)-N(3) = 104.8° for **81b** and N(2)-C(1)-N(1) = 104.3° for **90q**, are in good agreement with the value expected for a singlet *N*-heterocyclic carbene.[26]

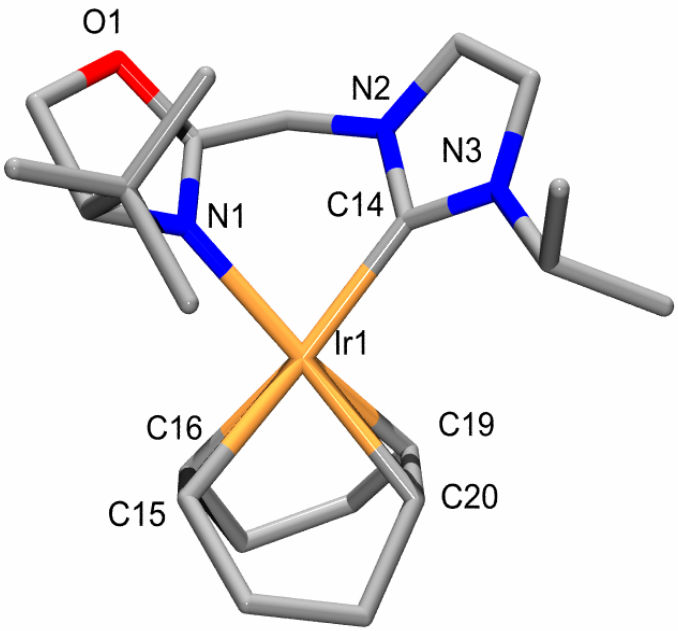


Figure 3.3 Structure of the cation of **81b**. Selected bond lengths (Å) and angles (°): Ir(1)-C(14) 2.034(4), Ir(1)-N(1) 2.089(4) Ir(1)-C(15) 2.175(3), Ir(1)-C(16) 2.193(4), Ir(1)-C(19) 2.105(5), Ir(1)-C(20) 2.136(3), C(15)-C(16) 1.388(6), C(19)-C(20) 1.418(7); N(2)-C(14)-N(3) 104.8(3), N(1)-Ir(1)-C(14) 82.28(15).

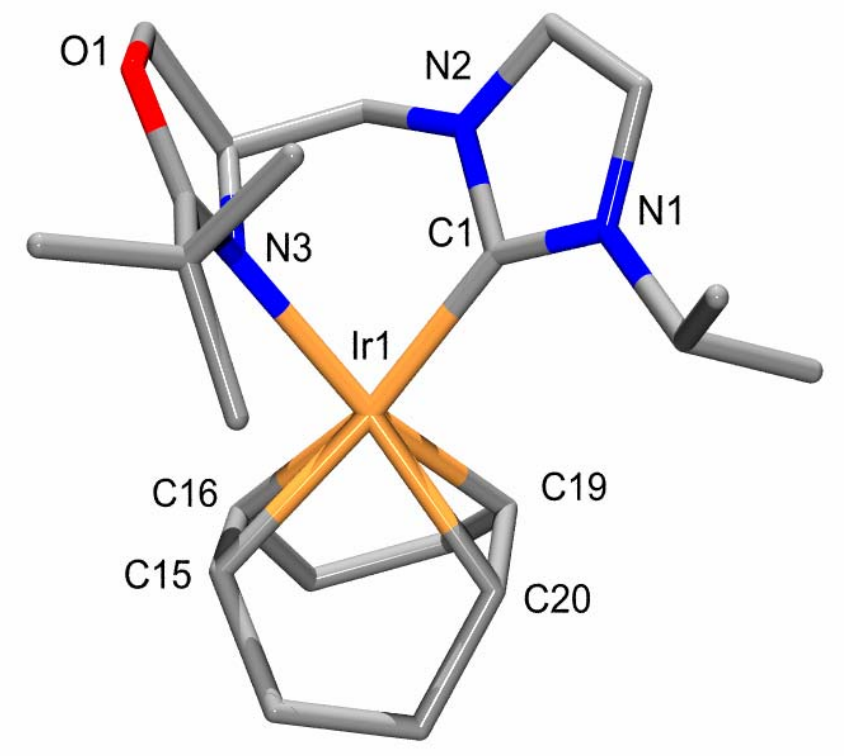


Figure 3.4 Structure of the cation of **90q**. Selected bond lengths (Å) and angles (°): Ir(1)-C(1) 2.042(3), Ir(1)-N(3) 2.094(2), Ir(1)-C(15) 2.159(3), Ir(1)-C(16) 2.167(3), Ir(1)-C(19) 2.115(3), Ir(1)-C(20) 2.124(3), C(15)-C(16) 1.383(6), C(19)-C(20) 1.403(5); N(2)-C(1)-N(1) 104.3(3), N(3)-Ir(1)-C(1) 79.47(11).

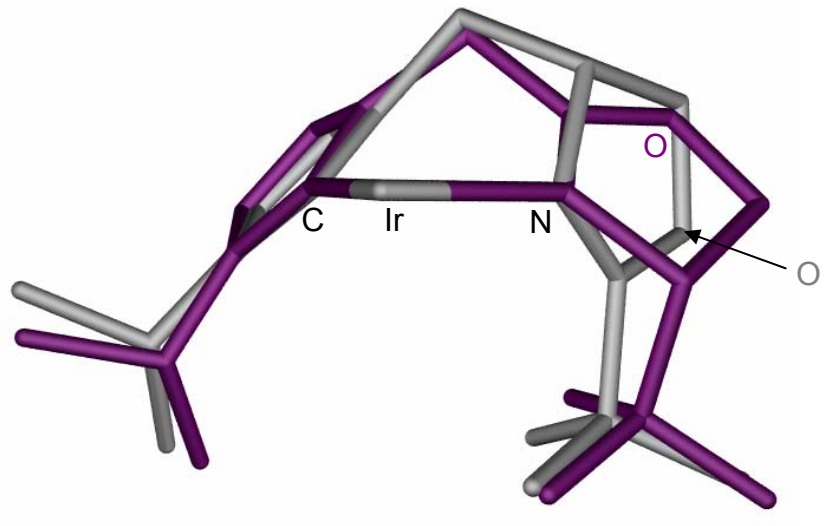
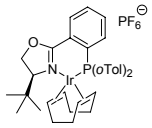
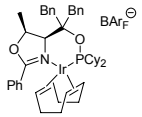
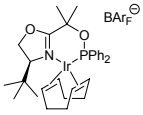
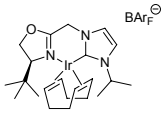
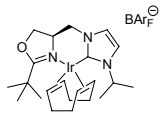


Figure 3.5 Superposition of the crystal structures of complex **81b** (purple) and **90q** (grey). The structures are aligned on the plane defined by the $C_{carbene}$-Ir-$N_{oxazoline}$ atoms. Counter-ion and cod omitted for clarity.

The ^{13}C-NMR chemical shifts of the cyclooctadiene olefinic C-atoms and the Ir-(C=C) distances *trans* to the oxazoline and *trans* to the NHC moiety were compared with those of the most efficient P,N-ligands developed in our laboratory (Table 3.1). According to the observed values, the *trans* influence of the imidazolin-2-ylidene group lies between that of the phosphine and the oxazoline groups. This is reflected by the Ir-(C=C) distances *trans* to the co-ordinating units, which increase from 200-204 pm for the oxazoline to 205-207 pm for the imidazolin-2-ylidene and 211-212 pm for the phosphine group.

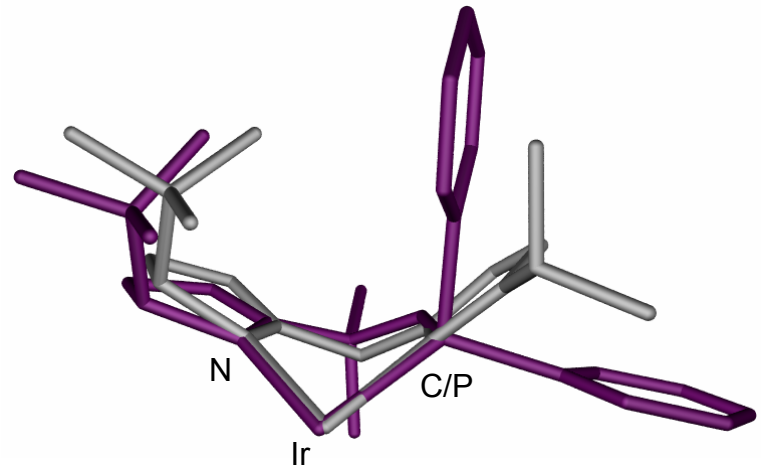
	Ir-(C=C) distance to Ir (pm)[a]		Ir-(C=C) ^{13}C NMR chemical shift[b]	
	trans to N	*trans* to P/C	*trans* to N	*trans* to P/C
 **91**	204	211	67.5 67.4	95.0 90.0
 **92**	203	212	69.2 64.9	102.8 96.6
 **93**	201	212	64.5 60.6	99.8 97.4
 **81b**	200	207	65.7 60.1	84.6 82.9
 **90b**	200[c]	205[c]	66.2 56.0	80.8 79.9

[a] distance from the midpoint of the cod double bond to Ir in pm. [b] chemical shift in ppm. [c] measured in complex **90q**.

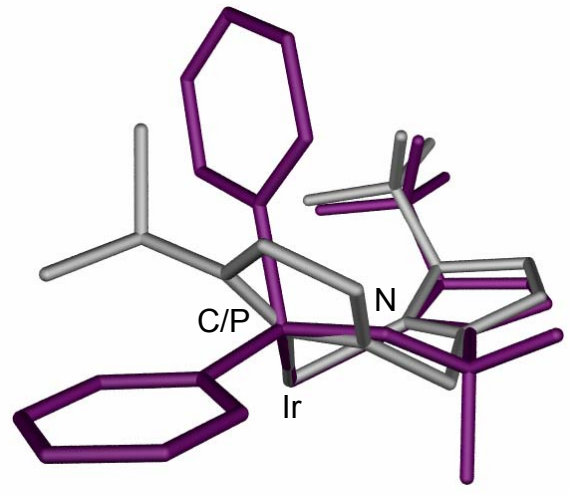
Table 3.1 Structural data of complexes **81b** and **90q** in comparison with complexes **91**,[27] **92**[28] and **93**.[29]

As shown by the superposition of the crystal structures of complexes **81b** and **90q**, the ligand arrangement around the iridium atoms in the two complexes is very similar (Figure 3.5). In both complexes, the six-membered chelate rings give rise to rigid structures with the R^1 and R^2 substituents pointing in the same direction.

In comparison to Ir-P,N complexes, in which the two substituents of the phosphine occupy a large region in space, the co-ordination sphere of Ir-**D** and Ir-**F** complexes is less shielded since the NHC moiety bears only one substituent. This difference in spatial occupation is highlighted in the superposition of the crystal structures of complexes **81b** and **93** (Figure 3.6).



Front view



Side view

Figure 3.6 Superposition of the crystal structures of complex **81b** (grey) and **93** (purple). The structures are aligned on the plane defined by the $N_{oxazoline}$-Ir-$C_{carbene}$ (**81b**) and the $N_{oxazoline}$-Ir-P atoms (Ir-A) atoms. Counter-ion and cod omitted for clarity.

3.5 Enantioselective hydrogenation

In order to investigate the potential of these complexes, we tested them in the asymmetric hydrogenation of four different unfunctionalised alkenes (**94**, **95**, **96** and **97**) and one α,β-unsaturated carboxylic ester (**98**) (Figure 3.7). For each substrate, our complexes were compared with Burgess' best catalyst **E1**, with R^1 = 1-adamantyl and R^2 = 2,6-diisopropylphenyl, and one threonine-derived phosphinite-oxazoline iridium complex (**92**). All reactions were set up under inert atmosphere with 1 mol% catalyst and 0.1 mmol of substrate in CH_2Cl_2 (0.5 ml).

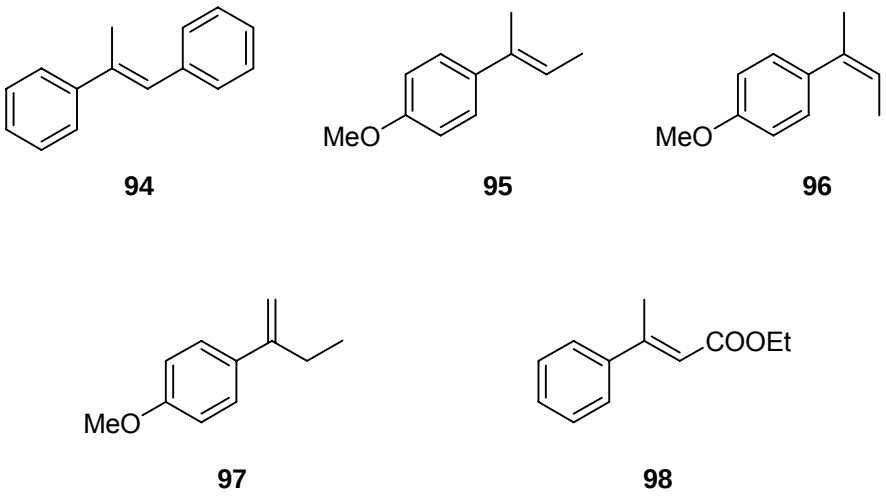
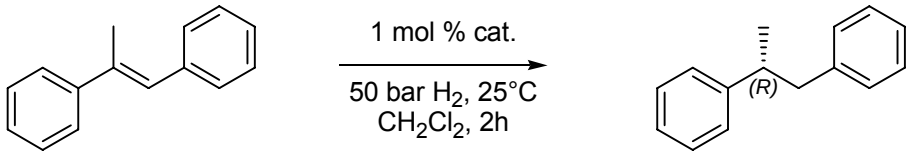


Figure 3.7 Substrates used in the hydrogenation screen.

In the hydrogenation of *trans*-α-methylstilbene **94**, up to 90% ee was obtained with the best catalysts of type **D** and **F** (**81a** and **90b**; Table 3.2). For type **D** catalysts (**81a-f**), the choice of R^1 = *tert*-butyl is crucial for activity as well as enantioselectivity. A decrease from 90% to 50% ee was observed when R^1 = *tert*-butyl was replaced by an isopropyl group. The strong influence of the oxazoline substituent is consistent with the findings of Burgess *et al*. for ligands of type **E**, which were rationalised by computational studies that suggested a strong steric interaction between the R^1 substituent and the substrate.[30] Although the R^2 substituent at the imidazolin-2-ylidene unit plays a less important role, the asymmetric induction increases when the size of R^2 is reduced (cf. complexes **81a**, **81c** and **81d**).



94

catalyst	R^1	R^2	yield[a]	ee[b]
81a	*t*Bu	Me	>99	90 (*R*)
81b	*i*Pr	Me	25[c]	55 (*R*)
81c	*t*Bu	*i*Pr	>99	87 (*R*)
81d	*t*Bu	2,4,6-$Me_3C_6H_2$	76	59 (*R*)
81e	*t*Bu	Neopentyl	96	84 (*R*)
81f	*t*Bu	Isobutyl	99	85 (*R*)
90a	*t*Bu	Me	>99	89 (*R*)
90b	*t*Bu	*i*Pr	>99	90 (*R*)
90c	*t*Bu	2,4,6-$Me_3C_6H_2$	>99	79 (*R*)
90d	*t*Bu	Neopentyl	>99	87 (*R*)
90e	*t*Bu	*t*Bu	66	78 (*R*)
90f	1-Ad	Me	97	69 (*R*)
90g	1-Ad	*i*Pr	>99	72 (*R*)
90h	1-Ad	2,4,6-$Me_3C_6H_2$	>99	61 (*R*)
90i	1-Ad	Neopentyl	>99	71 (*R*)
90j	1-Ad	*t*Bu	70	66 (*R*)
90k	2,6-$Me_2C_6H_3$	Me	27	68 (*R*)
90l	2,6-$Me_2C_6H_3$	*i*Pr	92	59 (*R*)
90m	2,6-$Me_2C_6H_3$	2,4,6-$Me_3C_6H_2$	15	rac.
90n	2,6-$Me_2C_6H_3$	Neopentyl	58	50 (*R*)
90o	2,6-$Me_2C_6H_3$	*t*Bu	7	32 (*R*)
E1[11]	1-Ad	2,6-*i*$Pr_2C_6H_3$	>99	98 (*S*)
92[4]	-	-	>99	99 (*R*)

[a] % Determined by GC. [b] % Determined by HPLC. [c] 5 mol% cat.

Table 3.2 Hydrogenation of *trans*-α-methylstilbene **94**.

Both activity and enantioselectivity of type **F** catalysts strongly depend on the oxazoline substituent. High conversion was obtained for R^1 = *tert*-butyl and 1-adamantyl, with the exception of complexes **90e** and **90j** bearing a *tert*-butyl group at the NHC unit. In these two catalysts, the co-ordination sphere seems to be too congested to allow high catalytic activity. With R^1 = 2,6-dimethylphenyl, activities were low to moderate (**90k**-**o**). As for the **D** series, the best enantioselectivities were recorded for catalysts with a *tert*-butyl group at the oxazoline ring (**90a**-**e**). Replacement of R^1 = *tert*-butyl by 1-adamantyl reduced the enantioselectivities by about 20%. With R^1 = 2,6-dimethylphenyl, the asymmetric induction was even lower. In combination with R^1 = *tert*-butyl, only the catalysts bearing small R^2 substituents such as methyl and isopropyl reached 90% ee, a trend already observed in the **D** series.

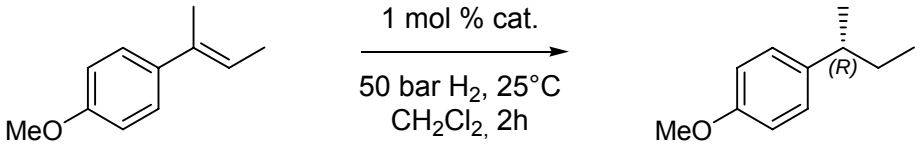
Hydrogenation of (*E*)-2-(4-methoxyphenyl)-2-butene **95** and (*Z*)-2-(4-methoxyphenyl)-2-butene **96** showed similar trends (Table 3.3 and 3.4). Contrary to *trans*-α-methylstilbene, the highest enantioselectivity values, 87% ee for alkene **95** and 73% ee for alkene **96**, were obtained with type **F** catalysts **90b** and **90c**, respectively.

Among type **D** catalysts, complex **81a**, which bears the least bulky substituent on the NHC ring, was again the most selective catalyst with 76% ee for substrate **95** and 56% ee for substrate **96**.

The results with type **F** catalysis confirmed the trend that the R^1 substituent has a strong influence on both activity and enantioselectivity. Similar to the hydrogenation of *trans*-α-methylstilbene, catalysts with R^1 = *tert*-butyl gave by far the highest enantiomeric excesses followed by catalysts with R^1 = 1-admantyl and R^1 = 2,6-dimethylphenyl. The R^2 substituent at the NHC unit allowed fine tuning of the enantioselectivity of substrates **95** and **96**. While the highest enantiomeric excesses were obtained for substrate **95** with a small R^2 group such as methyl (**90a**) and isopropyl (**90b**), the best enantioselectivities for substrate **96** were obtained with R^2 = 2,4,6-trimethylphenyl (**90c**).

Two further aspects of the hydrogenation of alkene **96** with Ir-**F** catalysts are remarkable. Firstly, three catalysts **90k**, **90l** and **90n** produce the opposite enantiomer. The observed formation of (*R*)-products starting from both the (*E*)- and the (*Z*)-olefins is in contrast to the general trend that (*E*)- and (*Z*)-olefins give products of opposite configuration.[5] A possible explanation could be that cis-trans isomerisation takes place during hydrogenation such that reactions of the less stable (*Z*)-isomer **96** proceed mainly via the (*E*)-isomer **95**.[31]

Secondly, catalysts **90e**, **90j** and **90o** with a *tert*-butyl group on the NHC moiety not only gave low conversion but also no asymmetric induction.

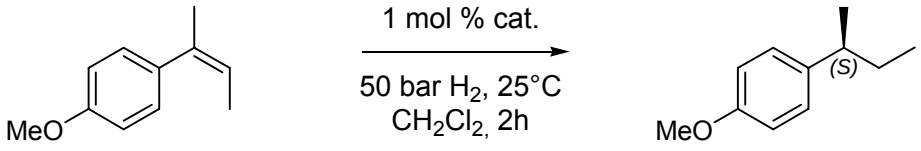


95

catalyst	R^1	R^2	yield[a]	ee[b]
81a	*t*Bu	Me	>99	76 (*R*)
81b	*i*Pr	Me	5	-
81c	*t*Bu	*i*Pr	>99	69 (*R*)
81d	*t*Bu	2,4,6-$Me_3C_6H_2$	>99	9 (*R*)
81e	*t*Bu	Neopentyl	>99	69 (*R*)
81f	*t*Bu	Isobutyl	>99	69 (*R*)
90a	*t*Bu	Me	>99	85 (*R*)
90b	*t*Bu	*i*Pr	>99	87 (*R*)
90c	*t*Bu	2,4,6-$Me_3C_6H_2$	>99	75 (*R*)
90d	*t*Bu	Neopentyl	>99	84 (*R*)
90e	*t*Bu	*t*Bu	50	80 (*R*)
90f	1-Ad	Me	>99	69 (*R*)
90g	1-Ad	*i*Pr	>99	71 (*R*)
90h	1-Ad	2,4,6-$Me_3C_6H_2$	>99	61 (*R*)
90i	1-Ad	Neopentyl	>99	73 (*R*)
90j	1-Ad	*t*Bu	87	75 (*R*)
90k	2,6-$Me_2C_6H_3$	Me	83	74 (*R*)
90l	2,6-$Me_2C_6H_3$	*i*Pr	89	59 (*R*)
90m	2,6-$Me_2C_6H_3$	2,4,6-$Me_3C_6H_2$	20	11 (*R*)
90n	2,6-$Me_2C_6H_3$	Neopentyl	84	61 (*R*)
90o	2,6-$Me_2C_6H_3$	*t*Bu	6	rac.
E1[11]	1-Ad	2,6-*i*$Pr_2C_6H_3$	>99	91 (*S*)
92[4]	-	-	>99	99 (*R*)

[a] % Determined by GC. [b] % Determined by HPLC.

Table 3.3 Hydrogenation of (*E*)-2-(4-methoxyphenyl)-2-butene **95**.



96

catalyst	R^1	R^2	yield[a]	ee[b]
81a	*t*Bu	Me	97	56 (*S*)
81b	*i*Pr	Me	3	- (*S*)
81c	*t*Bu	*i*Pr	>99	41 (*S*)
81d	*t*Bu	2,4,6-$Me_3C_6H_2$	65	27 (*S*)
81e	*t*Bu	Neopentyl	91	30 (*S*)
81f	*t*Bu	Isobutyl	97	46 (*S*)
90a	*t*Bu	Me	>99	56 (*S*)
90b	*t*Bu	*i*Pr	>99	66 (*S*)
90c	*t*Bu	2,4,6-$Me_3C_6H_2$	>99	73 (*S*)
90d	*t*Bu	Neopentyl	>99	50 (*S*)
90e	*t*Bu	*t*Bu	68	rac.
90f	1-Ad	Me	>99	33 (*S*)
90g	1-Ad	*i*Pr	>99	43 (*S*)
90h	1-Ad	2,4,6-$Me_3C_6H_2$	>99	66 (*S*)
90i	1-Ad	Neopentyl	>99	10 (*S*)
90j	1-Ad	*t*Bu	79	rac.
90k	2,6-$Me_2C_6H_3$	Me	89	25 (*R*)
90l	2,6-$Me_2C_6H_3$	*i*Pr	>99	38 (*R*)
90m	2,6-$Me_2C_6H_3$	2,4,6-$Me_3C_6H_2$	38	17 (*S*)
90n	2,6-$Me_2C_6H_3$	Neopentyl	>99	41 (*R*)
90o	2,6-$Me_2C_6H_3$	*t*Bu	18	rac.
E1[11]	1-Ad	2,6-*i*$Pr_2C_6H_3$	95	78 (*R*)
92[4]	-	-	>99	72 (*S*)

[a] % Determined by GC. [b] % Determined by HPLC.

Table 3.4 Hydrogenation of (*Z*)-2-(4-methoxyphenyl)-2-butene **96**.

The terminal olefin 2-(4-methoxyphenyl)-1-butene **97** is a much more reactive substrate than those discussed so far. Since previous work on substrate **97** showed that low hydrogen pressure increases the asymmetric induction,[5,32] catalyst screen was performed at 1 bar H_2 (Table 3.5).

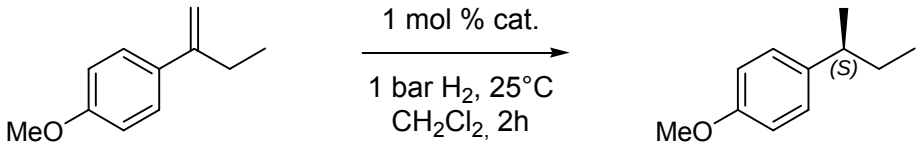
For type **D** catalysts, R^1 = *tert*-butyl is required for high activity. In this series, the importance of the R^2 substituent is demonstrated by a remarkable inversion of enantioselectivity from 15% ee (*R*) to 79% ee (*S*) when R^2 = methyl is replaced by an isopropyl group. With a value of 79% ee, complex **81c** was the most selective catalyst of both **81a-f** and **90a-o** libraries.

Type **F** catalysts gave low to moderate enantioselectivities. The best enantiomeric excesses of substrate **97** were again observed with R^1 = *tert*-butyl, even though the difference between the *tert*-butyl and the 1-adamantyl substituent is less pronounced than for substrates **94**, **95** and **96**. Complexes **90e**, **90j** and **90o**, bearing a *tert*-butyl substituent on the NHC moiety, showed no catalytic activity.

Finally, our catalyst library was tested in the hydrogenation of (*E*)-2-methylcinnamic acid ethyl ester **98** (Table 3.6). Type **D** complexes gave moderate enantioselectivities of up to 59% ee (**81a**). Complexes with less sterically hindered R^2 substituents such as methyl (**81a**), isopropyl (**81c**) and isobutyl (**81d**) were again the most enantioselective catalysts.

Higher enantioselectivities were obtained with catalysts of type **F**. Contrary to previous substrates **94**-**97**, the R^2 substituent in complexes **90a-j** plays a more important role than the R^1 substituent. The best enantiomeric excesses, 76% and 72% ee, were obtained with R^2 = 2,4,6-trimethylphenyl (**90c** and **90h**).

Moreover, in contrast to the results obtained with unfunctionalised alkenes, catalysts with R^1 = 1-adamantyl showed higher ee values than their analogues with R^1 = *tert*-butyl. With R^1 = 2,6-dimethylphenyl (**90k-o**), enantioselectivities were moderate. Contrary to catalysts **90a-j,** no positive effect on the asymmetric induction was observed with R^2 = 2,4,6-trimethylphenyl.

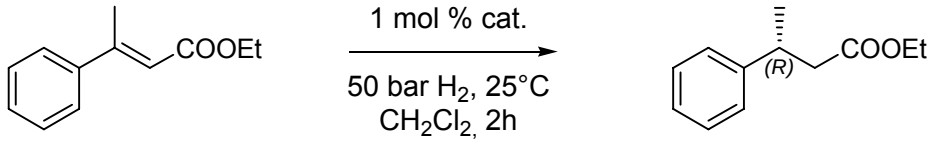


97

catalyst	R^1	R^2	yield[a]	ee[b]
81a	*t*Bu	Me	>99	15 (*R*)
81b	*i*Pr	Me	2	-
81c	*t*Bu	*i*Pr	>99	79 (*S*)
81d	*t*Bu	2,4,6-$Me_3C_6H_2$	>99	54 (*S*)
81e	*t*Bu	Neopentyl	>99	70 (*S*)
81f	*t*Bu	Isobutyl	>99	78 (*S*)
90a	*t*Bu	Me	>99	69 (*S*)
90b	*t*Bu	*i*Pr	>99	66 (*S*)
90c	*t*Bu	2,4,6-$Me_3C_6H_2$	>99	55 (*S*)
90d	*t*Bu	Neopentyl	>99	65 (*S*)
90e	*t*Bu	*t*Bu	0	-
90f	1-Ad	Me	>99	62 (*S*)
90g	1-Ad	*i*Pr	>99	56 (*S*)
90h	1-Ad	2,4,6-$Me_3C_6H_2$	>99	56 (*S*)
90i	1-Ad	Neopentyl	>99	65 (*S*)
90j	1-Ad	*t*Bu	0	-
90k	2,6-$Me_2C_6H_3$	Me	>99	29 (*S*)
90l	2,6-$Me_2C_6H_3$	*i*Pr	90	20 (*S*)
90m	2,6-$Me_2C_6H_3$	2,4,6-$Me_3C_6H_2$	20	rac.
90n	2,6-$Me_2C_6H_3$	Neopentyl	>99	27 (*S*)
90o	2,6-$Me_2C_6H_3$	*t*Bu	0	-
E1[11]	1-Ad	2,6-*i*$Pr_2C_6H_3$	>99	89 (*R*)
92[4]	-	-	>99	94 (*S*)

[a] % Determined by GC. [b] % Determined by HPLC.

Table 3.5 Hydrogenation of 2-(4-methoxyphenyl)-1-butene **97** at 1 bar H_2.



98

catalyst	R^1	R^2	yield[a]	ee[b]
81a	*t*Bu	Me	>99	59 (*R*)
81b	*i*Pr	Me	0	-
81c	*t*Bu	*i*Pr	>99	54 (*R*)
81d	*t*Bu	2,4,6-$Me_3C_6H_2$	93	13 (*S*)
81e	*t*Bu	Neopentyl	>99	48 (*R*)
81f	*t*Bu	Isobutyl	>99	55 (*R*)
90a	*t*Bu	Me	>99	12 (*R*)
90b	*t*Bu	*i*Pr	>99	38 (*R*)
90c	*t*Bu	2,4,6-$Me_3C_6H_2$	>99	72 (*R*)
90d	*t*Bu	Neopentyl	>99	30 (*R*)
90e	*t*Bu	*t*Bu	>99	rac.
90f	1-Ad	Me	>99	16 (*R*)
90g	1-Ad	*i*Pr	>99	46 (*R*)
90h	1-Ad	2,4,6-$Me_3C_6H_2$	>99	76 (*R*)
90i	1-Ad	Neopentyl	>99	44 (*R*)
90j	1-Ad	*t*Bu	96	36 (*R*)
90k	2,6-$Me_2C_6H_3$	Me	>99	50 (*R*)
90l	2,6-$Me_2C_6H_3$	*i*Pr	>99	41 (*R*)
90m	2,6-$Me_2C_6H_3$	2,4,6-$Me_3C_6H_2$	>99	30 (*R*)
90n	2,6-$Me_2C_6H_3$	Neopentyl	>99	27 (*R*)
90o	2,6-$Me_2C_6H_3$	*t*Bu	70	rac.
E1[11]	1-Ad	2,6-*i*$Pr_2C_6H_3$	-	-
92[4]	-	-	>99	94 (*R*)

[a] % Determined by GC. [b] % Determined by HPLC.

Table 3.6 Hydrogenation of (*E*)-2-methylcinnamic acid ethyl ester **98**.

3.6 Conclusion

Simple and efficient syntheses for two families of chiral iridium(oxazoline-carbene) complexes **D** and **F** with a six-membered chelate ring have been developed. The modular nature of these ligands allowed the preparation of a wide range of derivatives.

The complexes were tested in the iridium-catalysed asymmetric hydrogenation of olefins. Among type **D** complexes, catalyst **81a** gave the highest enantiomeric excesses for all substrates except terminal olefin **97**. Remarkably, catalyst **81a** is the one bearing the least bulky R^2 substituent at the NHC moiety.

The most selective catalysts in the **F** series were found to be equivalent or superior to type **D** complexes. Good enantioselectivities were generally induced by catalysts with a bulky *tert*-butyl- or adamantly-oxazoline unit in combination with a smaller group such as methyl or isopropyl at the NHC moiety. The functionalised substrate **98** is an exception. Here, the most efficient catalyst was complex **90h** bearing two bulky groups, 1-adamantyl and 2,4,6-trimethylphenyl.

The six-membered chelate complexes strongly differ from the seven-membered analogues **E** developed by Burgess. Whereas only one particular complex of type **E** was found to give high enantioselectivities, Ir-**E1** with R^1 = 1-adamantyl and R^2 = 2,6-diisopropylphenyl, several representatives of type **D** and **F** were identified, which induced similar ee levels. In contrast to Burgess' catalysts, which require large substituents at the NHC and oxazoline units for high enantioselectivity, the six-membered chelate analogues **D** and **F** in general give better results with less sterically demanding ligands.

However, despite the wide range of **D** and **F** type catalysts investigated, the enantiomeric excesses are not as high as those obtained with Burgess best complex Ir-**E1**. Nevertheless, our results indicate that carbene-oxazoline ligands of this type have considerable potential. Their modular nature, which enables easy tuning of the ligand structure suggests that they could find applications in other areas of asymmetric catalysis.

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Chapter 4

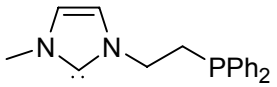
Phosphine/phosphinite-*N*-heterocyclic carbene ligands

4.1 Introduction

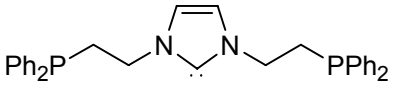
The disposition of the phosphine substituents in the Ir-P,N complexes is thought to be crucial for high asymmetric induction.[1] In chapter three, a crystal structure comparison of iridium oxazoline-imidazolin-2-ylidene complexes with Ir-PHOX showed that the spatial occupation of the imidazolin-2-ylidene moiety (which has been considered by Nolan and co-workers as "fences" with a defined length and height)[2] strongly differs from that of the phosphine moiety. Whereas NHC shields the co-ordination sphere with only one substituent, the phosphine with two substituents occupies a much larger region in space. Moreover, in comparison to NHCs, phosphines are versatile ligands, whose steric and electronic parameters can be easily modulated.[3]

In order to take advantage of the properties that phosphines show in iridium-asymmetric hydrogenation, we decided to synthesise chiral ligands in which a NHC is tethered to a phosphine or a phosphinite moiety.

Phosphine-NHC bidentate ligands have been already investigated by Herrmann, who published in 1996 the first achiral phosphine-NHC ligand **99**, obtained by reduction of the corresponding phosphine oxide using methyldichlorosilane (Figure 4.1). Ruthenium complexes were prepared but no catalytic reaction was reported.[4] A few years later, applications of achiral phosphine-NHC ligands to palladium cross-coupling reactions were investigated by Nolan[5,6] and Lee.[7] Recently, tridentate phosphine-NHC pincer ligand, $PC^{NHC}P$ **100**, was developed and successfully used in ruthenium-catalysed transfer hydrogenation.[8,9]



99

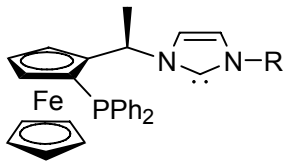


100

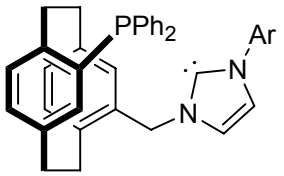
Figure 4.1 First achiral phosphine-NHC **99** and tridentate $PC^{NHC}P$ ligands **100**.

The first chiral phosphine-NHC ligand was published in 2003 by Chung who took advantage of the ferrocene backbone to synthesise ligand **101** (Figure 4.2).[10] A paracyclophane backbone was used by Bolm to prepare ligand **102,** iridium complexes of which were tested in the asymmetric catalytic hydrogenation of olefins.[11] The complexes showed low activities and low enantioselectivities. Ligand **103**, developed by Helmchen, gave high asymmetric induction in the rhodium-catalysed hydrogenation of dimethyl itaconate and *N*-acetyldehydroamino acid derivatives.[12] More recently, Togni prepared chiral phosphine-NHC

pincer ligand **104** and undertook some preliminary studies in the palladium catalysed enantioselective addition of morpholine to methacrylonitrile.[13,14]



101



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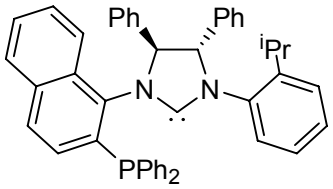

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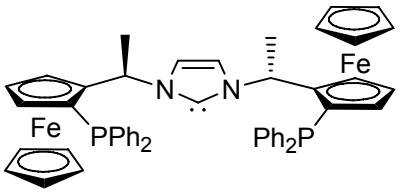
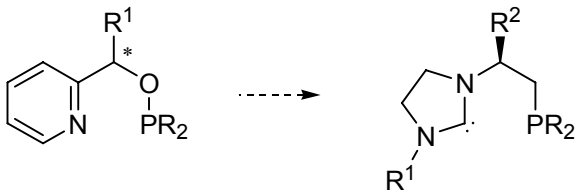


104

Figure 4.2 Chiral phosphine-NHC and tridentate $PC^{NHC}P$ ligands.

The first phosphine-NHC ligand that we decided to synthesise was derived from pyridyl phosphinite ligands **105**, recently developed in our group (Figure 4.3). Pyridyl-phosphinite ligands **105** are efficient ligands for the iridium-catalysed asymmetric hydrogenation of olefins. The success achieved with this simple structure, in which the stereogenic centre is situated at the bridge between the pyridine moiety and the phosphinite, prompted us to synthesise structural analogue phosphine-NHC ligands **106**. Contrary to pyridyl-phosphinite ligands **105**, phosphine-NHC ligands **106** have a R^1 substituent which points towards the co-ordination sphere of iridium, thus allowing fine-tuning of the steric hindrance in close proximity to the metal.

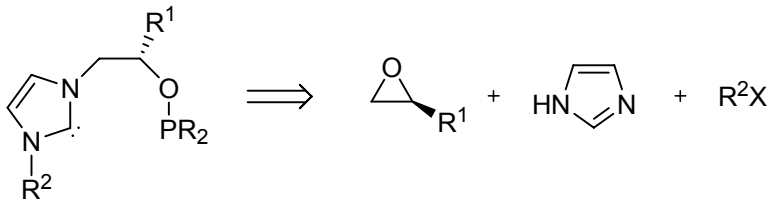


105 **106**

Figure 4.3 Derivation of phosphine-NHC ligands with a stereogenic centre at the chelate ring.

In a closely related project, we synthesised phosphinite-NHC ligands **107** (Figure 4.4). Phosphinite-NHC **107** should be readily available from commercially available chiral

epoxides **108**. This synthesis allows easy variation of the chirality centre, the imidazolin-2-ylidene substituents and the phosphinite moiety.



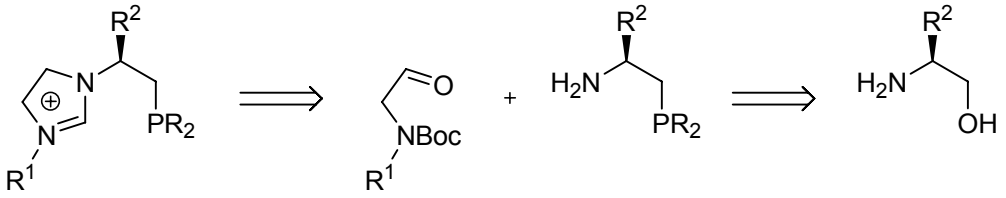
107 **108**

Figure 4.4 Synthesis of phosphinite-NHC ligands **107** from chiral epoxides.

4.2 Phosphine-*N*-heterocyclic carbene ligands

4.2.1 Ligand design and synthesis

Synthesis of phosphine-imidazolium salts **109**, precursors to phosphine-NHC ligands **106**, is not straightforward, since introduction of a phosphine group almost always requires basic conditions that might interfere with imidazolium salts. We therefore decided to build the imidazolium salt moiety after synthesis of the phosphine (Figure 4.5). Previously reported amino-phosphines **111**,[15,16] derived from amino-alcohols **112**, were found to be a convenient building block for this synthesis, since the imidazolium salt moiety could be introduced via the primary amine functionality in a three step synthesis according to a procedure reported by Hoveyda.[17]



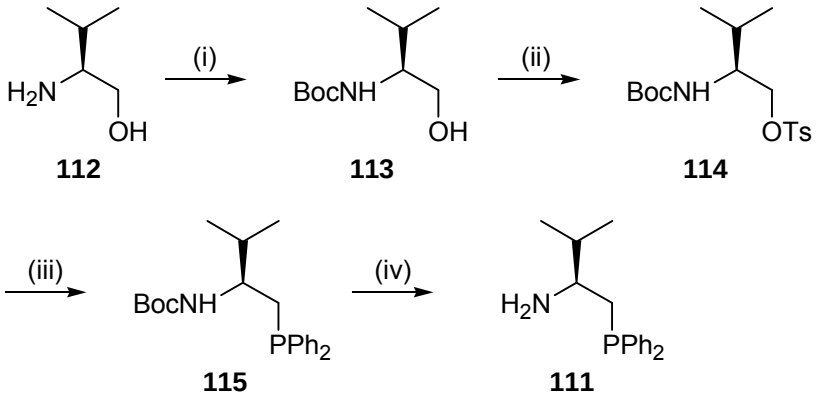
109 **110** **111** **112**

Figure 4.5 Retrosynthesis of phosphine-imidazolium salt **109**.

The synthesis of amino-phosphine **111** (R^2 = *i*Pr), which was investigated by Björn Gschwend during his Wahlpraktikum work, is described in Scheme 4.1. Minor modifications were added to the reported procedure.

Boc-protection of amino-alcohol **112** yielded alcohol **113**, which was subsequently converted to tosylate **114** using tosyl chloride and triethylamine in CH_2Cl_2. Despite its tendency to

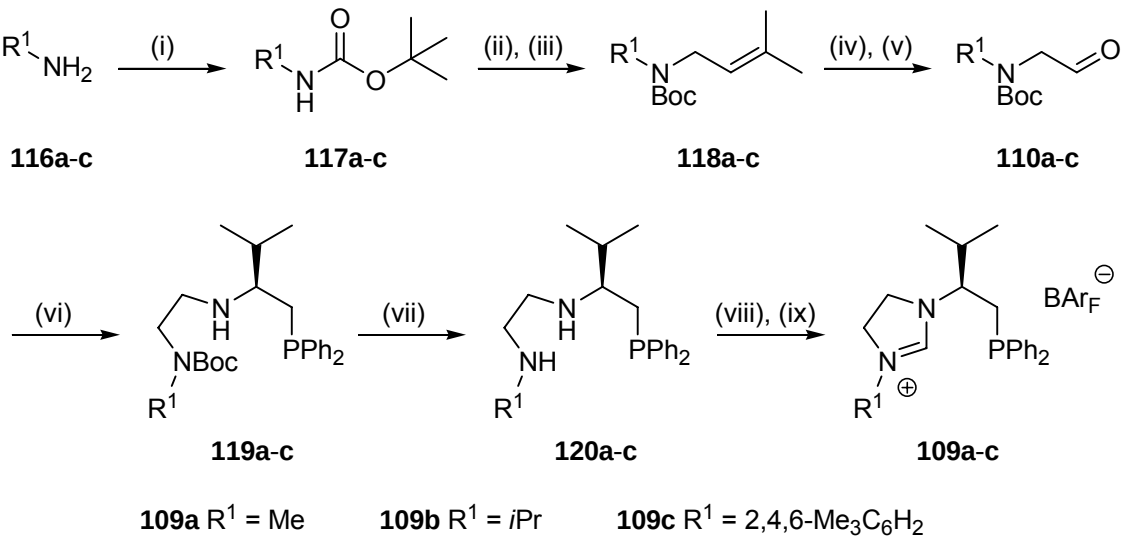
undergo intramolecular cyclisation, tosylate **114** was purified by chromatography on silica gel and was further reacted with a solution of $KPPh_2$ in THF at -35°C. Finally, Boc-deprotection of phosphine **115** yielded the desired amino-phosphine **111** in 31% overall yield.



Reagents and conditions: (i) $(Boc)_2O$, NEt_3, CH_2Cl_2, 25°C, (95%), 15h; **(ii)** TsCl, NEt_3, CH_2Cl_2, -10°C→25°C, RT, 8h, (55%); **(iii)** $KPPh_2$, THF, -35°C, 15h, (58%); **(iv)** TFA, CH_2Cl_2, RT, 20h, (99%);

Scheme 4.1 Synthesis of amino-phosphine **111**.

Following a procedure developed by Hoveyda, aldehydes **110** were prepared from primary amines **116a-c** (Scheme 4.2).



109a R^1 = Me **109b** R^1 = *i*Pr **109c** R^1 = 2,4,6-$Me_3C_6H_2$

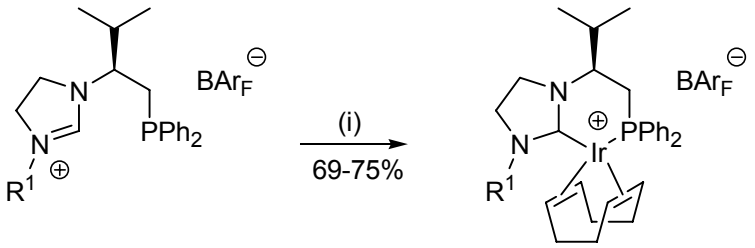
Reagents and conditions: (i) $(Boc)_2O$, DMAP (1 mol%), THF, RT, 19h, (55-74%); **(ii)** KH, DMF, 0°C→25°C, 2h; **(iii)** 3,3-dimethylallylbromide, DMF, RT, 1h, (30-74% over two steps); **(iv)** O_3/O_2, MeOH and CH_2Cl_2 (1:3), -78°C, ½h; **(v)** Me_2S, RT, 3h, (74-82% over two steps); **(vi)** amino-phosphine **111**, $NaHB(OAc)_3$, CH_2ClCH_2Cl, RT, 4h, (74-82%); **(vii)** TFA, CH_2Cl_2, RT, 20h, (82-99%); **(viii)** $HC(OEt)_3$, NH_4BF_4, 100°C, 1h; **(ix)** $NaBAr_F$, CH_2Cl_2, RT, 15 min, (48-80%).

Scheme 4.2 Synthesis of phosphine-imidazolium salts **109a-c**.

Boc-protection of amines **116** yielded carbamates **117**, which were deprotonated using KH in DMF and then subjected to nucleophilic substitution with 3,3-dimethylallylbromide to give olefins **118**. Since olefins **118** were not stable on silica gel, the crude products were directly converted into aldehydes **110** by ozonolysis using dimethyl sulfide. Reductive amination of aldehydes **110** with amino-phosphine **111**, gave phosphine **119** in 74-82% yield. Boc-deprotection followed by ring-closure using NH_4BF_4 and $HC(OEt)_3$ yielded imidazolium salts bearing a tetrafluoroborate counter-ion. Similar to the procedure developed to purify oxazoline-imidazolium salts (see chapter three), BF_4^- counter-ion exchange with BAr_F^- allowed purification of phosphine-imidazolium salts **109** by chromatography on silica gel. To prevent phosphine oxidation, reactions and purification procedures of compounds **119**, **120** and **109** were performed under inert atmosphere. Three different phosphine-imidazolium salts **109a-c** with R^1 = Me, *i*Pr and 2,4,6-$Me_3C_6H_2$ were prepared by this method.

4.2.2 Iridium complexes synthesis and structural analysis

Iridium complexes **121a-c** were obtained by deprotonation of the corresponding imidazolium salts with freshly sublimed NaO*t*Bu in presence of the metal precursor, $[(\eta^4\text{-cod})IrCl]_2$ (see chapter three). Upon addition of NaO*t*Bu, a fast colour change from yellow to dark red was observed (Scheme 4.3).



109a-c **121a-c**

121a R^1 = Me **121b** R^1 = *i*Pr **121c** R^1 = 2,4,6-$Me_3C_6H_2$

Reagents and conditions: (i) $[(\eta^4\text{-cod})IrCl]_2$, NaO*t*Bu, THF, RT, 2h.

Scheme 4.3 Synthesis of iridium complexes **121a-c**.

Complexes **121a-c** were fully characterised by 2D NMR techniques. Single crystals suitable for X-ray analysis were obtained for complexes **122b** and **122c**, analogues of complexes **121b** and **121c** bearing BF_4^- as counter-ion. Complexes **122b** and **122c** were prepared by the same

procedure as previously described, but the reaction was performed with the crude BF_4^- imidazolium salts instead of BAr_F^- imidazolium salts **109b** and **109c**.

In order to give insight into the structural characteristics and the dynamic behaviour of complexes **121a-c**, a detailed analysis of complex **121c** will be presented here. At room temperature, complex **121c** showed broad signals in the ^{1}H-NMR spectrum and two peaks in the ^{31}P-NMR spectrum at $\delta = 3.18$ ppm (major) and $\delta = 6.35$ ppm (minor) with a 2:1 ratio. Clearly, two species are present in solution. At -25°C, the signals were sharp enough and full NMR analyses allowed the assignment of structure **121c** to both species. Particular care was taken to prove the co-ordination mode of the imidazol-2-ylidene at the N*C*N position of the ring for both species. At -25°C, the two conformers interconvert, as proved by the cross-peaks observed in the NOESY spectrum. Since no interconversion was observed for the two *ortho*-methyl groups of the mesityl ring, rotation of the imidazol-2-ylidene substituent as origin of the conformers was ruled out. The geometry of the two conformers was difficult to assign unequivocally with NOESY spectrum. However, an important observation was made, when the isopropyl substituent on the chelate ring of the major conformer showed a NOE to one olefinic proton of the cod moiety.

Further structural information about complex **121c** was obtained by analysing the crystal structure of its analogue **122c**, which is depicted in Figure 4.6.

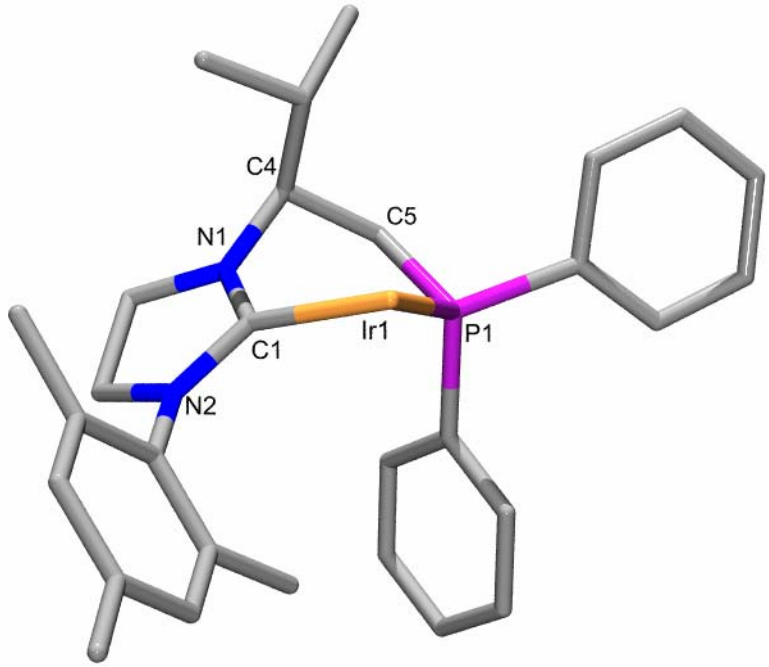
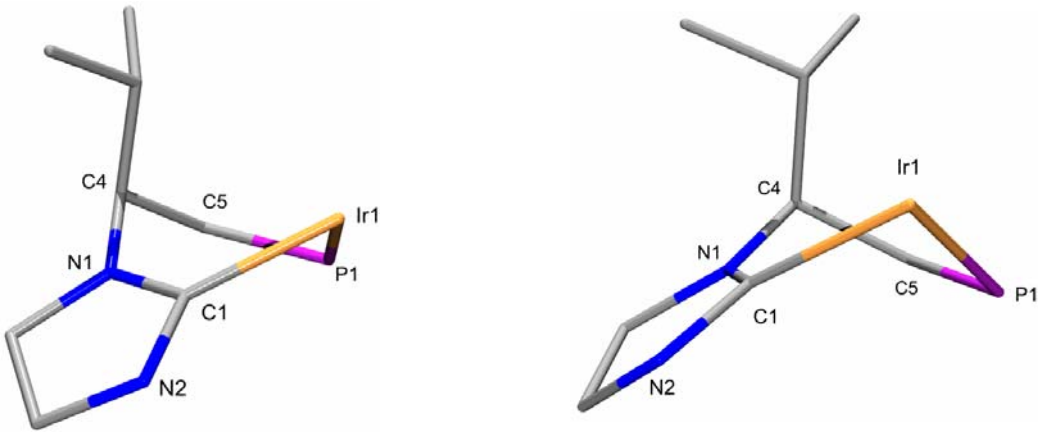


Figure 4.6 Crystal structure of complex **122c**. Counter-ion and cod omitted for clarity. Ir(1)-C(1) 2.0606(19), Ir(1)-P(1) 2.3034(4), N(1)-C(1)-N(2) 107.50(17).

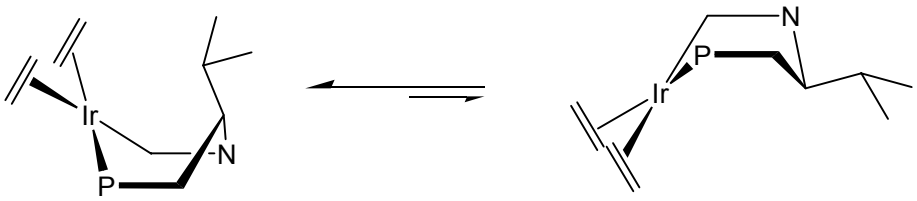
The bond angle at the carbene centre N(1)-C(1)-N(2) = 107.5°C is in good agreement with that expected for a singlet *N*-heterocyclic carbene.[18] The iridium atom lies in an almost square planar arrangement, with the cod double bonds perpendicular to the plane of coordination.
The chelate ring around the iridium has a boat-like conformation. Such geometry is expected with this type of ligand, since the planarity of the NHC moiety forces the C(4), N(1), C(1) and Ir(1) atoms to lie in the same plane (measured torsion angle = 3.9°C). This geometry best fits with a boat conformation of the six-membered chelate ring (Figure 4.7).



Side view Front view

Figure 4.7 Boat-like conformation origin in complex **122c**.

From a structural point of view, a boat-like geometry of the chelate ring allows complex **121c** to adopt two conformations (Figure 4.8). In the first conformation (**a**), which corresponds to the crystal structure of **122c**, the isopropyl substituent is bent over the iridium and in the second conformation (**b**), it is pointing away from the metal.



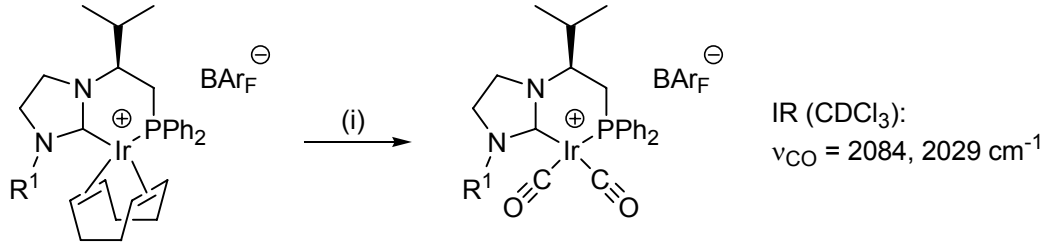
(**a**) (**b**)

Figure 4.8 The two possible arrangements of complex **121c**. Cyclooctadiene double bonds shown for clarity.

This hypothesis is consistent with the two conformers observed by NMR. In solution, the major conformer, which shows a NOE between one olefinic proton of the cod and the

isopropyl group, would correspond to structure (**a**). Structure (**b**) would be therefore the minor conformer.

Dicarbonyl derivative **123c** was prepared from complex **121c** in order to investigate the influence of cod on the conformers' equilibrium. Dicarbonyl complex **123c** was obtained by dissolving complex **121c** in $CDCl_3$ and stirring under 1 bar of CO at room temperature for 30 minutes (Scheme 4.4). A few seconds after pressurisation of the reaction vessel with CO, the colour changed from dark red to light yellow.



121c **123c**

Reagents and conditions: (i) CO 1 bar, $CDCl_3$, RT, 30 min.

Scheme 4.4 Synthesis of dicarbonyl complex **123c**.

^{1}H-NMR confirmed complete loss of cod. In the ^{31}P-NMR spectrum, one signal at $\delta = 1.56$ ppm was observed at room temperature. Even though NMR measurements indicate the presence of one species in solution, one can not exclude the fact that, without cod, the equilibrium of the two conformers is too fast to be observed on the NMR-time scale. Therefore, one can not unequivocally conclude that complex **123c** has one conformer in solution.

Similar to complex **121c**, complexes **121a** and **121b** have two conformers in solution at room temperature, as observed by NMR. However, the absence of cross-peaks in the NOESY spectrum proved that the conformers did not interconvert. The crystal structure of **122b** (which is the analogue of **121b** bearing BF_4^- as counter-ion) showed the same arrangement of the ligand around the iridium as that of complex **122c** (Figure 4.9).

Observation of conformers for complexes **121a**, **121b** and **121c** highlights the lack of rigidity of phosphine-carbene ligand **106**. Therefore, with such a ligand backbone, dynamic behaviour of the chelate ring is likely to affect the chirality transfer from the catalyst to the substrate during hydrogenation.

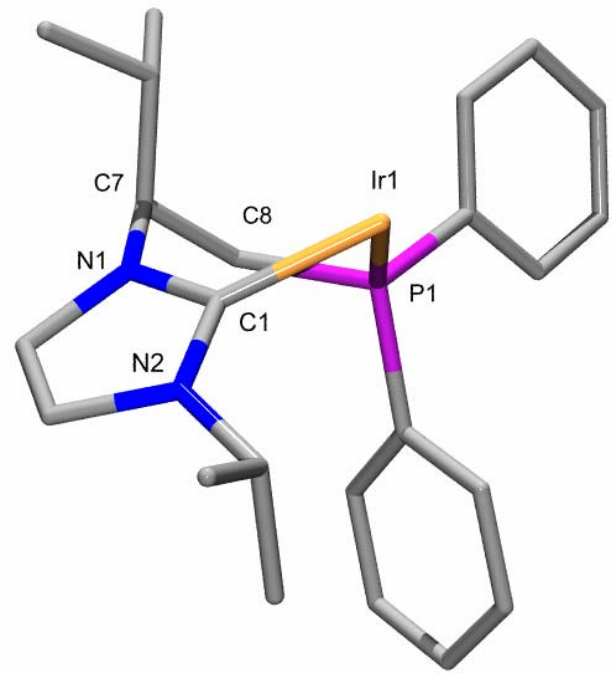


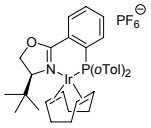
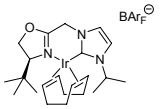
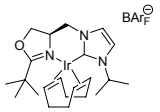
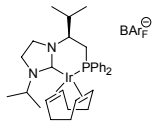
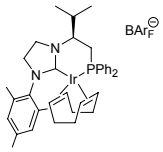
Figure 4.9 Crystal structure of complex **122b**. Counter-ion and cod omitted for clarity. Ir(1)-C(1) 2.0606(19), Ir(1)-P(1) 2.3034(4), N(1)-C(1)-N(2) 107.50(17).

The electronic properties of complexes **121b** and **121c** were investigated by measuring the ^{13}C-NMR chemical shift of the cod olefinic C-atoms and the distance from the cod double bonds to iridium (Ir-(C=C) *trans* to the carbene and *trans* to the phosphine (Table 4.1). Complexes **121b** and **121c** were compared with oxazoline-imidazolin-2-ylidene complexes **81b** and **90b** (see chapter three) and Ir-PHOX **91**.

There is a small difference between the imidazolin-2-ylidene unit of complexes **81b** and **90b** and the imidazol-2-ylidene unit of complexes **121b** and **121c**. In comparison to imidazolin-2-ylidene, imidazol-2-ylidene has no aromaticity which can stabilise the carbene, and therefore induces a larger *trans* influence. This is illustrated by a longer Ir-C=C distance and a larger chemical shift of the cod olefinic C-atoms *trans* to C in complexes **121b** and **121c**.

According to the data for complexes **91**, **81b** and **90b**, the diphenylphosphine group has the strongest *trans* influence, followed by imidazolin-2-ylidene and then oxazoline. This order is unexpected, since NHC have been proven to be a better donor than phosphines (see introduction). In complexes **121b** and **121c**, a direct and therefore more accurate comparison of the phosphine and the imidazol-2-ylidene group can be made, since the two are present in the same complex. As shown in the crystal structure of complexes **122b** and **122c**, the Ir-C=C distances *trans* to the phosphine and the imidazol-ylidene are in the same range (207-209

ppm). Moreover, the ^{13}C-NMR signals of the olefinic C-atoms of complexes **121b** and **121c** all resonate in the same region, between 79-90 ppm.

	Ir-(C=C) distance to Ir[a]		Ir-(C=C) ^{13}C-NMR chemical shift[b]	
	trans to N	*trans* to P/C	*trans* to N	*trans* to P/C
 **91**	204	211	67.5 67.4	95.0 90.0
 **81b**	200	207	65.7 60.1	84.6 82.9
 **90b**	200[c]	205[c]	66.2 56.0	80.8 79.9
	trans to C	*trans* to P	*trans* to C	*trans* to P
 **121b**	208[d]	209[d]	88.9 / 81.9 major 90.1 / 87.1 minor	84.0 / 81.5 major 79.2 / 79.3 minor
 **121c**	209[e]	207[e]	88.8 / 87.2 major 86.5 / 83.6 minor	78.9 / 77.8 major 81.5 / 82.5 minor

[a] distance from the midpoint of the cod double bond to Ir in pm. [b] chemical shifts in ppm. [c] measured in complex **90q**. [d] measured in complex **122b**. [e] measured in complex **122c**.

Table 4.1 Structural comparison of iridium complex **121b** and **121c** with oxazoline-imidazol-2-ylidene iridium complex **81b** and **90b** and Ir-PHOX **91**.

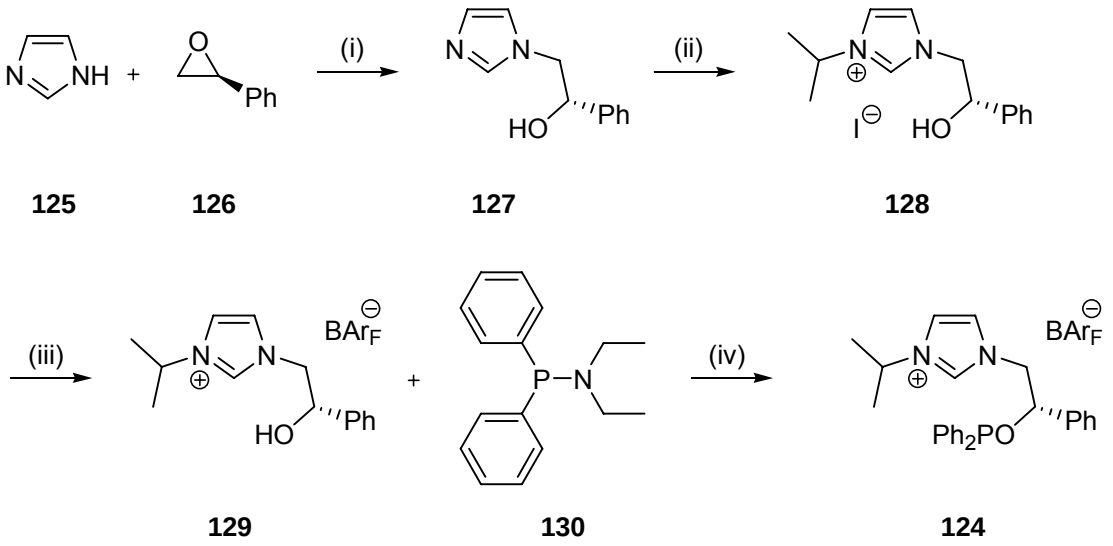
More important, in comparison to Ir-PHOX complex **91**, which shows significant differentiation between the two cod double bonds, complexes **121b** and **121c** have almost no C=C electronic imbalance.

4.3 Phosphinite-*N*-heterocyclic carbene ligands

4.3.1 Ligand design and synthesis

As shown in the preceding section, the synthesis of phosphine-imidazolium salts is subject to functional group tolerance issues. Since the basic conditions generally needed to synthesise a phosphine are incompatible with imidazolium salts, the latter must be introduced at the end of the ligand synthesis. However, synthesising the phosphine first is not very attractive. Firstly, variation of the phosphine substituents requires much more synthetic work and secondly, precautions to avoid phosphine oxidation are required throughout the synthesis.

A solution to this problem was found by synthesising phosphinite-imidazolium salt **124** (Scheme 4.5). Synthesis of a phosphinite moiety, which can be achieved via the corresponding alcohol using mild phosphorylating reagents, should be possible in presence of imidazolium salts and, therefore, was the last step of the ligand synthesis.



125 **126** **127** **128**

129 **130** **124**

Reagents and conditions: (i) neat, 50°C, 12h; **(ii)** *i*PrI, CH_3CN, 80°C, 3h, (30% over two steps); **(iii)** $NaBAr_F$, CH_2Cl_2, 15 min, (83%); **(iv)** 4,5-dichloroimidazole, NEt_3, CH_2Cl_2, RT, 48h, (60%).

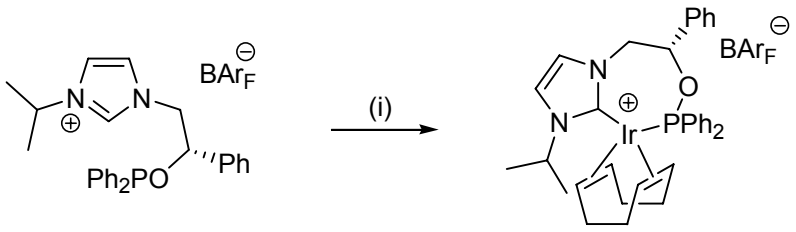
Scheme 4.5 Synthesis of phosphinite-imidazolium salt **124**.

Synthesis of alcohol-*N*-heterocyclic-imidazolium **128** was achieved in a one-pot procedure, as reported in the literature.[19-22] Purification of imidazolium salt **128** by crystallisation from hot acetonitrile was tedious and accounted for the low yield of the procedure. Counter-ion exchange with $NaBAr_F$, gave BAr_F^- imidazolium salt **129** in good yield. The BAr_F^- counter-ion was introduced at this stage of the synthesis to enhance the solubility of imidazolium salt **129** in dichloromethane, which was crucial for the next step in the synthesis. Phosphorylation

of the alcohol was achieved using diphenylphosphamide **130**[23] in combination with NEt_3 and 4,5-dichloroimidazole as catalyst. The reaction required 1.5 equivalents of phosphamide to yield phosphinite **124** in 60% within 48 hours. Purification of phosphinite **124** by chromatography was only possible using alox (Fluka, adjusted to grade III). On silica gel, the phosphinite was hydrolysed back to alcohol **129**.

4.3.2 Iridium complex synthesis and structural analysis

Complexation of phosphinite-imidazolium salt **124** was achieved by deprotonation with NaO*t*Bu in the presence of $[(\eta^4\text{-cod})IrCl]_2$ (Scheme 4.6). The orange complex was purified by chromatography on silica gel. The degree of purity of phosphinite-imidazolium salt **124** was important in order to obtain a clean complex. A test experiment, in which the crude phosphinite-imidazolium salt was used for complexation, yielded complex **131** with impurities that could not be separated by chromatography.



124 **131**

Reagents and conditions: (i) $[(\eta^4\text{-cod})IrCl]_2$, NaO*t*Bu, THF, RT, 2h, (69%).

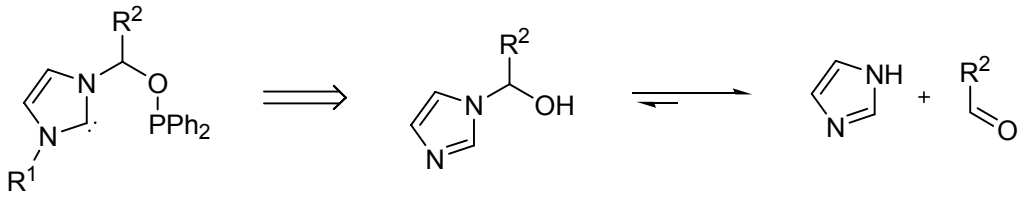
Scheme 4.6 Synthesis of iridium complex **131**.

2D NMR analyses of complex **131** showed the presence of two species in solution. Assignment of the two structures confirmed that they were conformers (5:1 ratio), but no interconversion was observed by NOESY. NOESY data seem to indicate that, similar to the phosphine-imidazolin-2-ylidene complexes, the two conformers arise from a flip of the chelate ring.

Comparison of the ^{13}C-NMR chemical shifts of the cod olefinic C-atoms (89.0 ppm and 95.7 ppm *trans* to P; 79.5 ppm and 81.1 ppm *trans* to C) suggested that the phosphine and the imidazolin-2-ylidene moieties of complex **131** have a comparable *trans* influence similar to complex **121b-c** (see Table 4.1).

4.3.3 Attempted synthesis of a C(5) activated phosphinite-NHC iridium complex

In iridium-catalysed hydrogenation, Ir-P,N complex with six-membered ring have proven to be the catalyst of choice.[24] We were therefore interested in designing a phosphinite-NHC ligand with a six-membered chelate ring. A conventional approach would have been synthesis of ligands **132** depicted in Figure 4.10. However, such structure is not easily accessible given the instability of the corresponding alcohols **133**, which are known to decompose to aldehydes **134** and 1*H*-imidazole.



132 **133** **134**

Figure 4.10 Ligand **132**: synthetic issues.

A possible solution to this problem was suggested by the work of Crabtree on abnormal binding modes of NHCs.[25-27] As already presented in the introduction, Crabtree recently reported that metalation of imidazolium salts can occur, under specific conditions, at C(5) instead of C(2). As depicted in Figure 4.11, synthesis of a phosphinite-imidazolium salt with a C(5) binding mode would solve the problem of the alcohol precursor instability. In order to ensure chelation at the C(5) position, C(2) protection of the phosphinite-imidazolium salts with R = alkyl or aryl was envisaged.

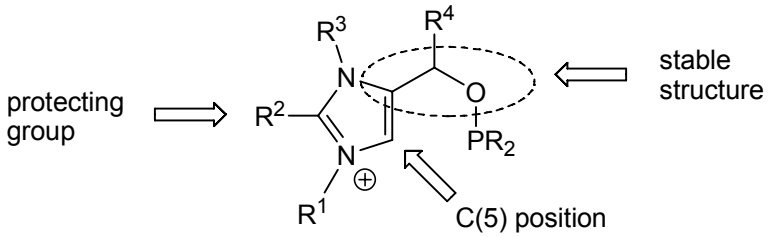
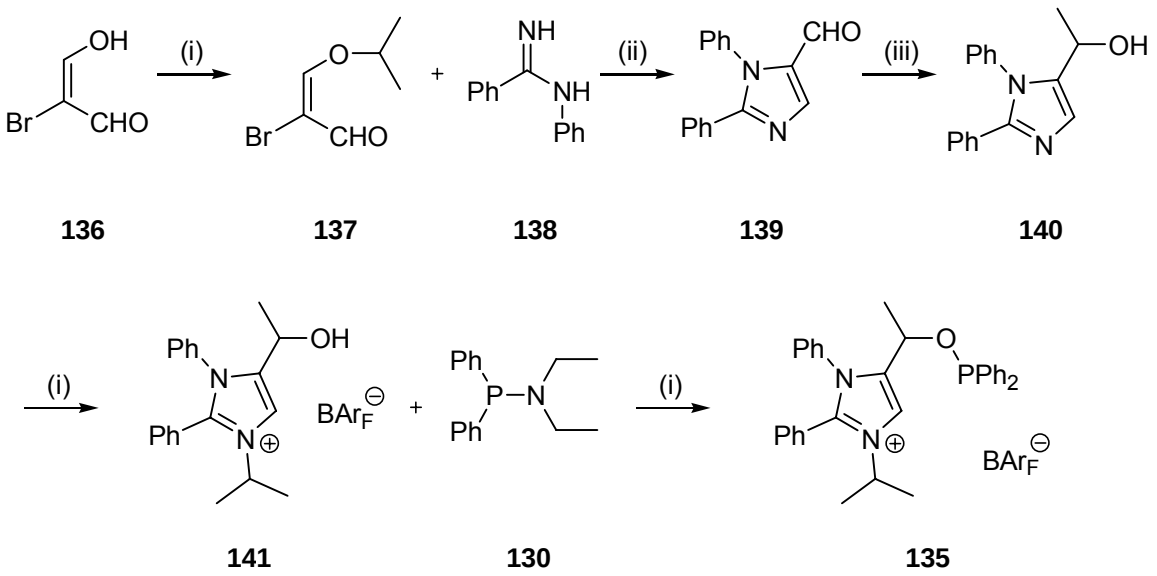


Figure 4.11 Design of phosphinite-imidazolium salt with a six-membered chelate ring.

Synthesis of phosphinite-imidazolium salt **135** is depicted in Scheme 4.7. The key compound of the synthesis, imidazolecarbaldehyde **139**, was synthesised in two steps, according to a literature procedure.[28] Activation of bromomalonaldehyde **136**, followed by condensation

with *N*-phenylbenzamidine **138** gave imidazolecarbaldehyde **139** in 77% overall yield. This reaction is quite remarkable since only one regioisomer is obtained. Aldehyde **139** was converted into alcohol **140** by Grignard reaction. Subsequent alkylation of imidazole using isopropyliodide, followed by counter-ion exchange using $NaBAr_F$ yielded imidazolium salt **141**. The latter was purified by chromatography on silica gel. Phosphinite **135** was synthesised using diphenylphosphamide in combination with NEt_3 and 4,5-dichloroimidazole and purified by chromatography on alox (Fluka, adjusted to grade III).



Reagents and conditions: (i) *i*PrOH, PTSA (cat.), cyclohexane, 100°C, ½h; **(ii)** K_2CO_3, $CHCl_3$ and H_2O (8:1), RT, 10h, (77%); **(iii)** MeMgCl, THF, -78°C→RT, 12h, (85%); **(iv)** *i*PrI, DMF, 95°C, 18h; **(v)** $NaBAr_F$, CH_2Cl_2, 15 min, (19% over two steps); **(vi)** 4,5-dichloroimidazole, NEt_3, CH_2Cl_2, RT, 48h, (91%).

Scheme 4.7 Synthesis of phosphinite-imidazolium salt **135**.

Complexation of phosphinite-imidazolium **135** proved to be more difficult than expected. Addition of NaO*t*Bu to a solution of $[(\eta^4\text{-cod})IrCl]_2$ and phosphinite-imidazolium salt **135** in THF did not yield the desired chelate complex. After chromatography on silica gel, the ^{13}C-NMR spectrum of the complex obtained (**142**) showed no signal in the region where carbene signals are expected (150-210 ppm). Moreover, ESI-MS of complex **142** proved that the C(5) position was not deprotonated using the conditions described above. Four species were observed by ESI-MS (Figure 4.12). The heaviest one had a mass-to-charge ratio m/z = 828.1 corresponding to complex **143**. The signal at m/z = 719.2 was attributed to structure **143** without cod. Phosphinite-imidazolium salt **135** was observed at m/z = 491.3 and one product **145** from decomposition of the ligand showed a signal at m/z = 289.3. As shown

by coupled MS-MS experiments, the three lightest species arose from complex **143** fragmentation during measurement. Since the chloride counter-ion in complex **143** can come either from the iridium precursor $[(\eta^4\text{-cod})IrCl]_2$ or from the ESI-MS instrument, it is not possible to assign unequivocally structure **143** to complex **142**.

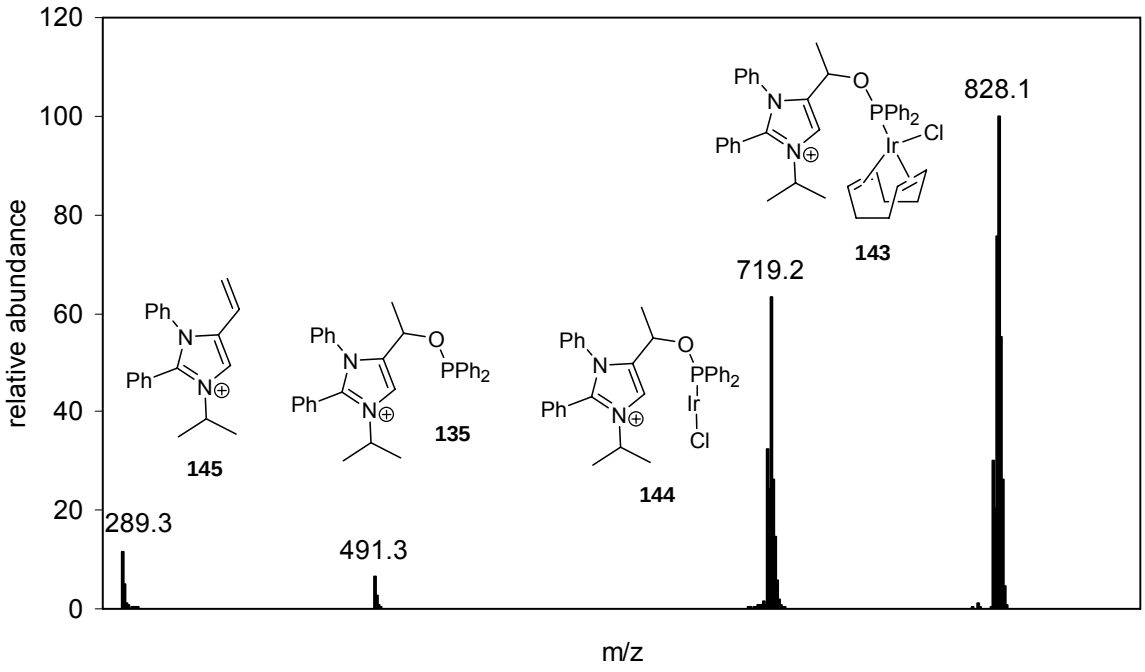


Figure 4.12 ESI-MS spectrum of complex **142**.

Metalation at the C(5) position is thermodynamically much less favoured than at C(2).[25] Several methodologies were therefore investigated in order to activate the C(5) position. Stronger bases than NaO*t*Bu, such as *n*BuLi, BEMP and $KN(Si(CH_3)_3)_2$, the latter being the most efficient in the formation of acyclic diaminocarbene,[29] were tested without success. Transmetalation via silver complexes was also investigated, but no complex formation with silver was observed when Ag_2O was reacted with phosphinite-imidazolium salt **135**.

4.4 Hydrogenation

Phosphine carbene iridium complexes **121a**, **121b** and **121c** and phosphinite-carbene complex **131** were tested in the iridium-catalysed hydrogenation of five unfunctionalised olefins (**146-150**), two functionalised olefins (**151** and **152**) and one imine (**153**) depicted in Figure 4.13.

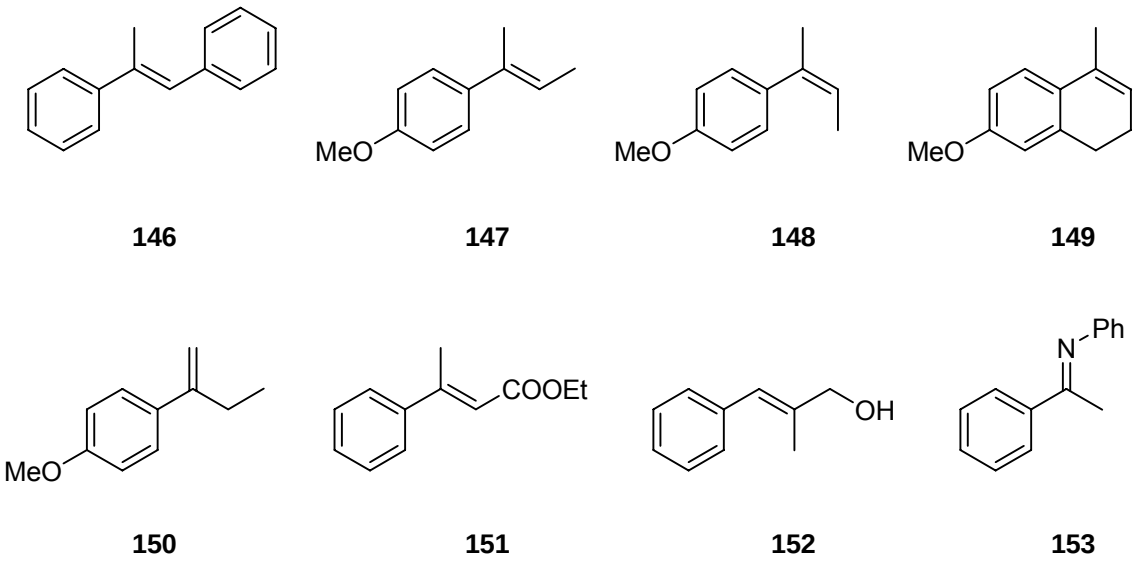


Figure 4.13 Substrates tested in the hydrogenation screen.

In order to compare the results, all reactions were set up under inert atmosphere with 1 mol% catalyst and 0.1 mmol substrate in 0.5 ml of CH_2Cl_2.

*Unfunctionalised trisubstituted olefins **146-149***

Initial investigations of our catalysts were undertaken with unfunctionalised trisubstituted olefins **146-149** (Table 4.2-4.5). It quickly became apparent that our catalysts were not very active in comparison to the usual Ir-P,N complexes, for which TOF values up to 5000 h^{-1} were measured for the hydrogenation of *trans*-α-methylstilbene.[30] Twelve hours were not enough for substrates **146-149** to be fully hydrogenated. The lowest activities were measured with *trans*-α-methylstilbene **146** with conversion values as low as to 12% after 12 hours. Generally, phosphinite complex **131** was more active than phosphine complexes **121a**, **121b** and **121c**. Low asymmetric induction was observed for all four catalysts. The highest enantiomeric excess (63%) was obtained by using catalyst **121c** for the hydrogenation of *trans*-α-methylstilbene.

catalyst	time (h)	pressure (bar)	*N* subst.	conversion (%)[a]	ee (%)[b]
121a	12	50	Me	10	rac.
121b	12	50	*i*Pr	21	5 (*R*)
121c	12	50	2,4,6-$Me_3C_6H_2$	38	63 (*R*)
131	12	50	*i*Pr	12	6 (*R*)

[a] % Determined by GC. [b] Determined by HPLC.

Table 4.2 Hydrogenation of *trans*-α-methylstilbene **146** at 50 bar H_2.

catalyst	time (h)	pressure (bar)	*N* subst.	conversion (%)[a]	ee (%)[b]
121a	12	50	Me	68	rac.
121b	12	50	*i*Pr	80	rac.
121c	12	50	2,4,6-$Me_3C_6H_2$	77	36 (*R*)
131	12	50	*i*Pr	>99	rac.

[a] % Determined by GC. [b] Determined by HPLC.

Table 4.3 Hydrogenation of (*E*)-2-(4-methoxyphenyl)-2-butene **147** at 50 bar H_2.

catalyst	time (h)	pressure (bar)	*N* subst.	conversion (%)[a]	ee (%)[b]
121a	12	50	Me	52	5 (*S*)
121b	12	50	*i*Pr	68	rac.
121c	12	50	2,4,6-$Me_3C_6H_2$	61	10 (*S*)
131	12	50	*i*Pr	95	15 (*R*)

[a] % Determined by GC. [b] Determined by HPLC.

Table 4.4 Hydrogenation of (*Z*)-2-(4-methoxyphenyl)-2-butene **148** at 50 bar H_2.

catalyst	time (h)	pressure (bar)	*N* subst.	conversion (%)[a]	ee (%)[b]
121a	12	50	Me	29	14 (*R*)
121b	12	50	*i*Pr	38	28 (*R*)
121c	12	50	2,4,6-$Me_3C_6H_2$	18	rac.
131	12	50	*i*Pr	93	5 (*R*)

[a] % Determined by GC. [b] Determined by HPLC.

Table 4.5 Hydrogenation of 7-methoxy-4-methyl-1,2-dihydro-naphtalene **149** at 50 bar H_2.

*Unfunctionalised disubstituted olefin **150***

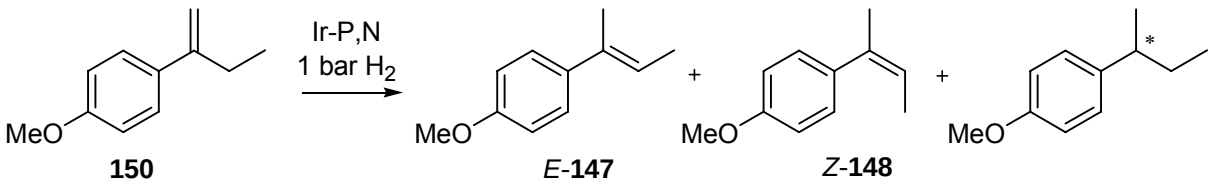
The catalysts were then tested with terminal olefin **150**, which is known to be easily hydrogenated.[1,31] Under the same conditions described above, full conversion was obtained with all the complexes (Table 4.6). The enantiomeric excesses measured were again very low and with catalyst **121a** and **131**, a racemic mixture of the product was obtained.

catalyst	time (h)	pressure (bar)	*N* subst.	conversion (%)[a]	ee (%)[b]
121a	12	50	Me	>99	rac.
121b	12	50	*i*Pr	>99	5 (*S*)
121c	12	50	2,4,6-$Me_3C_6H_2$	>99	13 (*S*)
131	12	50	*i*Pr	>99	rac.

[a] % Determined by GC. [b] Determined by HPLC.

Table 4.6 Hydrogenation of 2-(4-methoxyphenyl)-1-butene **150** at 50 bar H_2.

Since olefin **150** is known to give higher enantioselectivities when hydrogenated at low pressure, we reduced the hydrogen pressure to 1 bar. Under such conditions, double bond isomerisation was observed. At the end of the reaction, a mixture of olefin **150**, *E*-isomer **147**, *Z*-isomer **148** and the product was observed (Scheme 4.8, Table 4.7).



150 *E*-**147** *Z*-**148**

Scheme 4.8 Hydrogenation of substrate **150** at 1 bar H_2.

catalyst	time (h)	*Z* (%)[a]	*E* (%)[a]	product (%)[a]	ee (%)[b]
121a	2	15	12	10	13 (*R*)
121b	2	16	9	7	-
121c	2	22	8	11	22 (*S*).
131	2	7	4	0	-

[a] % Determined by GC. [b] Determined by HPLC.

Table 4.7 Hydrogenation of 2-(4-methoxyphenyl)-1-butene **150** at 1 bar H_2.

*Ester functionalised olefin **151***

Higher activity was observed during hydrogenation of (*E*)-2-methylcinnamic acid ethyl ester, which was fully hydrogenated in 12 hours by all the catalysts (Table 4.8). When the reaction time was reduced to three hours, catalysts **121b** and **121c** still achieved full conversion. The asymmetric induction was however low. The highest ee value (43%) was measured with catalyst **121b** bearing an isopropyl group on the imidazol-2-ylidene.

catalyst	time (h)	pressure (bar)	*N* subst.	conversion (%)[a]	ee (%)[b]
121a	12	50	Me	>99	20 (*S*)
121b	12	50	*i*Pr	>99	43 (*S*)
121c	12	50	2,4,6-$Me_3C_6H_2$	>99	6 (*S*)
131	12	50	*i*Pr	>99	11 (*S*)
121a	6	50	Me	87	20 (*S*)
121b	6	50	*i*Pr	>99	43 (*S*)
121c	6	50	2,4,6-$Me_3C_6H_2$	>99	10 (*S*)
131	6	50	*i*Pr	78	7 (*S*)
121a	3	50	Me	35	9 (*S*)
121b	3	50	*i*Pr	>99	43 (*S*)
121c	3	50	2,4,6-$Me_3C_6H_2$	>99	10 (*S*)
131	3	50	*i*Pr	39	rac.

Table 4.8 Hydrogenation of (*E*)-2-methylcinnamic acid ethyl ester **151** at 50 bar H_2.

*Alcohol functionalised olefin **152***

Hydrogenation of alcohol functionalised olefin **152** was then investigated. The activities were higher than those observed for ester functionalised olefin **151**. After 3 hours at 50 bar H_2, full conversion was obtained for every catalysts (Table 4.9). The best asymmetric induction (42%) was obtained with catalyst **121b** bearing an isopropyl substituent on the imidazol-2-ylidene. When the reaction time was reduced to 15 minutes, catalysts **121a** and **121b** still achieved full conversion. The high activities observed prompted us to perform a pressure dependence study of the catalysts. Three hydrogen pressures, 100 bar, 20 bar and 10 bar were investigated (Table 4.10). At 10 bar H_2, the activities were still acceptable, even though only catalyst **121b** gave full conversion. In terms of asymmetric induction, increasing the pressure resulted in an increase of enantioselectivity. A considerable increase in ee was observed for catalyst **121b**, which almost doubled its enantioselectivity when the hydrogen pressure was raised from 10 bar (24% ee) to 100 bar (43% ee).

catalyst	time (h)	pressure (bar)	*N* subst.	conversion (%)[a]	ee (%)[b]
121a	3	50	Me	>99	37 (-)
121b	3	50	*i*Pr	>99	42 (-)
121c	3	50	2,4,6-$Me_3C_6H_2$	>99	26 (-)
131	3	50	*i*Pr	>99	23 (+)
121a	1	50	Me	>99	35 (-)
121b	1	50	*i*Pr	>99	42 (-)
121c	1	50	2,4,6-$Me_3C_6H_2$	>99	26 (-)
131	1	50	*i*Pr	71	20 (+)
121a	15 min.	50	Me	>99	39 (-)
121b	15 min.	50	*i*Pr	>99	41 (-)
121c	15 min.	50	2,4,6-$Me_3C_6H_2$	86	27 (-)
131	15 min.	50	*i*Pr	31	18 (+)

[a] % Determined by GC. [b] Determined by HPLC.

Table 4.9 Hydrogenation of (*E*)-2-methyl-3-phenyl-prop-2-en-1-ol **152** at 50 bar H_2.

catalyst	time (h)	pressure (bar)	*N* subst.	conversion (%)[a]	ee (%)[b]
121a	1	100	Me	>99	39 (-)
121b	1	100	*i*Pr	>99	43 (-)
121c	1	100	2,4,6-$Me_3C_6H_2$	>99	28 (-)
131	1	100	*i*Pr	83	24 (+)
121a	3	20	Me	>99	27 (-)
121b	3	20	*i*Pr	>99	33 (-)
121c	3	20	2,4,6-$Me_3C_6H_2$	85	20 (-)
131	3	20	*i*Pr	>99	20 (+)
121a	3	10	Me	85	26 (-)
121b	3	10	*i*Pr	>99	24 (-)
121c	3	10	2,4,6-$Me_3C_6H_2$	74	17 (-)
131	3	10	*i*Pr	51	16 (+)

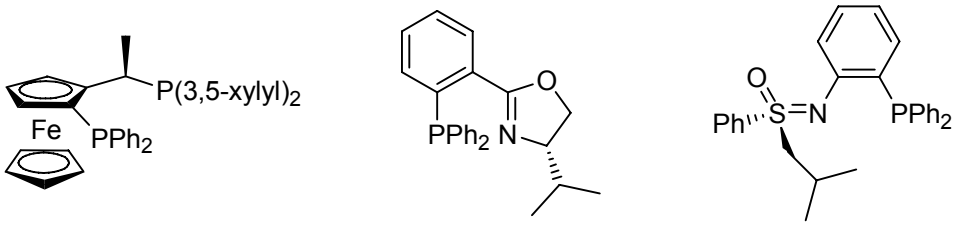
[a] % Determined by GC. [b] Determined by HPLC.

Table 4.10 Pressure dependence study of (*E*)-2-methyl-3-phenyl-prop-2-en-1-ol **152**.

*Imine **153***

High enantioselectivity and high turnover frequency (TOF) has proved difficult to achieve in the hydrogenation of acyclic *N*-arylamines.[32] Imines have some peculiarities that makes their stereoselective hydrogenation more difficult than that of alkenes. They are often sensitive to hydrolysis; the presence of *syn*/*anti* isomers requires the catalyst to reduce all isomers with the same sense of enantioselectivity, and the product can co-ordinate to the catalyst thus reducing its activity.

Among all the systems developed so far, three are noteworthy (Figure 4.14). The first one, catalyst Ir-**154** in the presence of iodide and acids, which was developed for the hydrogenation of an intermediate for the Syngenta herbicide (1*S*)-Metolachlor, TOFs reached up to 200'000 h^{-1} and ee values of 80%.[33] The second one, iridium catalyst Ir-PHOX **155** with a BAr_F^- counter-ion, gave a TOF up to 2'820 h^{-1} and up to 81% ee in supercritical CO_2.[34] More recently, Bolm developed sulfoxime phosphine ligand **156**, which iridium complex in combination with iodide gave ee values of up to 96% with good activities.[35]



154 **155** **156**

Figure 4.14 Chiral ligands used in iridium-catalysed asymmetric hydrogenation of imines.

The last substrate of our screen was imine **153**. As a reference value, 0.1 mol% Ir-**155** complex hydrogenates imine **153** in less than 15 minutes with an ee value of 89%. Similar to the alcohol functionalised substrate **152**, the catalysts showed generally good activities (Table 4.11). In one hour at 50 bar H_2, catalysts **121a**, **121b** and **131** fully hydrogenated imine **153**. The substituent on the imidazol-2-ylidene plays an important role in terms of asymmetric induction. An increase from 6% (*S*) to 46% (*R*) ee was observed when R^1 = methyl was replaced by an isopropyl group.

catalyst	time (h)	pressure (bar)	*N* subst.	conversion (%)[a]	ee (%)[b]
121a	3	50	Me	>99	6 (*S*)
121b	3	50	*i*Pr	>99	47 (*R*)
121c	3	50	2,4,6-$Me_3C_6H_2$	39	rac.
131	3	50	*i*Pr	>99	46 (*S*)
121a	1	50	Me	>99	6 (*S*)
121b	1	50	*i*Pr	>99	49 (*R*)
121c	1	50	2,4,6-$Me_3C_6H_2$	18	rac.
131	1	50	*i*Pr	>99	46 (*S*)
121a	15 min.	50	Me	>99	6 (*S*)
121b	15 min.	50	*i*Pr	53	59 (*R*)
121c	15 min.	50	2,4,6-$Me_3C_6H_2$	6	rac.
131	15 min.	50	*i*Pr	>99	48 (*S*)

[a] % Determined by GC. [b] Determined by HPLC.

Table 4.11 Hydrogenation of imine **153** at 50 bar H_2.

A hydrogen pressure dependence study was performed with imine **153** (Table 4.12). At 10 bar H_2, 3 hours were enough for catalysts **121a**, **121b** and **131** to achieve full conversion. Varying the pressure affected the enantioselectivity of only catalyst **121b**. Contrary to alcohol functionalised substrate **152**, increasing the pressure resulted in an decrease of enantioselectivity. A good correlation between the pressure and the enantioselectivity was found, as depicted in Figure 4.15. The highest enantiomeric excess (60% ee) was obtained with catalyst **121b** at 10 bar H_2 in three hours.

catalyst	time (h)	pressure (bar)	*N* subst.	conversion (%)[a]	ee (%)[b]
121a	1	100	Me	>99	7 (*S*)
121b	1	100	*i*Pr	>99	34 (*R*)
121c	1	100	2,4,6-$Me_3C_6H_2$	19	rac.
131	1	100	*i*Pr	>99	46 (*S*)
121a	3	20	Me	>99	6 (*S*)
121b	3	20	*i*Pr	>99	57 (*R*)
121c	3	20	2,4,6-$Me_3C_6H_2$	42	rac.
131	3	20	*i*Pr	>99	47 (*S*)
121a	3	10	Me	>99	7 (*S*)
121b	3	10	*i*Pr	98	60 (*R*)
121c	3	10	2,4,6-$Me_3C_6H_2$	31	rac.
131	3	10	*i*Pr	>99	48 (*S*)

[a] % Determined by GC. [b] Determined by HPLC.

Table 4.12 Pressure dependence study of imine **153**.

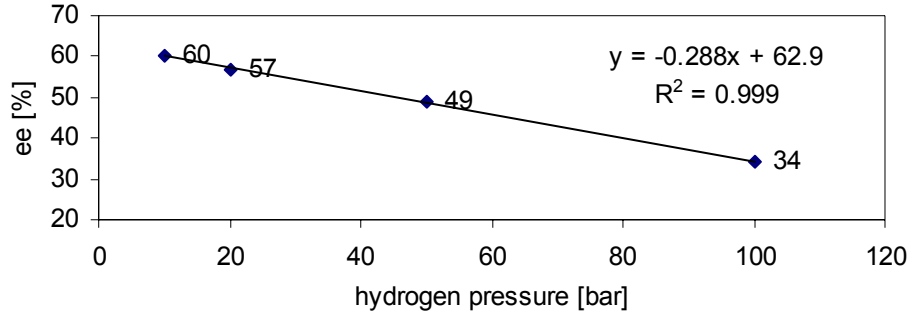


Figure 4.15 Hydrogen pressure dependence of catalyst **121b** enantioselectivity.

4.5 Conclusion

Three chiral phosphine-imidazol-2-ylidene iridium complexes have been synthesised starting from amino-phosphine **111**. As shown by NMR analysis, the three complexes exist as two conformers in solution at room temperature. 2D NMR analysis and X-ray diffraction studies of complex **121b**, bearing a mesityl substituent on the imidazol-2-ylidene, showed that the conformers arose from a flip of the six-membered chelate ring. The electronic properties of complexes **121b** and **121c** were investigated by measuring the ^{13}C-NMR chemical shifts of the cod olefinic C-atoms and the distance from the cod double bonds to iridium (Ir-(C=C) *trans* to the carbene and *trans* to the phosphine). In contrast to Ir-P,N complexes, almost no difference of the *trans* influence exerted on the two cod double bonds was observed.

Phosphinite-carbene ligands were also investigated. A four step synthesis for phosphinite-imidazolin-2-ylidene ligands was established starting from chiral epoxides. Using this procedure, one complex was prepared. 2D NMR analysis showed that this complex displays two conformers in solution at room temperature.

In order to gain access to phosphinite-carbene complexes with a six-membered chelate ring, preparation of phosphinite ligands containing a NHC unit with a carbenoid centre at C(5) was attempted. Synthesis of the achiral imidazolium salt precursor was achieved in six steps. Despite investigating many complexation methods, activation of the C(5) position of the imidazolium salt was not possible.

Iridium complexes **121a**, **121b**, **121c** and **131** were tested in the catalytic hydrogenation of olefins. Unfunctionalised olefins were difficult to hydrogenate. Twelve hours at 50 bar H_2 were not enough for the catalysts to achieve full conversion. The asymmetric inductions observed were generally low. Much higher activities were measured when functionalised olefins **151** and **152** were hydrogenated. Alcohol functionalised olefin **152** was fully hydrogenated in one hour at 50 bar H_2 by almost all catalysts. The highest enantiomeric excesses (42% ee for ester olefin **151** and 43% ee for alcohol olefin **152**) were obtained by phosphine-imidazol-2-ylidene complex **121b** with R^1 = isopropyl.

Similar to functionalised olefins, imine **153** was fully hydrogenated at 50 bar H_2 in one hour by almost all catalysts. The highest enantiomeric excess, 47% ee, which was obtained with phosphine-imidazol-2-ylidene complex with R^1 = isopropyl, was improved to 60% ee by reducing the pressure to 10 bar H_2.

The difference in reactivity observed between unfunctionalised olefins and α,β-unsaturated ester **151**, allylic alcohol **152** and imine **153** emphasises the fact that the electronic properties

of the phosphine/phosphinite-carbene iridium complexes are considerably different from those of Ir-P,N complexes. The good activities (TOF up to 400 h^{-1}) measured for the functionalised substrates are encouraging, in particular for imines, which remain difficult substrates to hydrogenate with high asymmetric induction and good TOF.

The enantiomeric excesses measured throughout the screen are rather disappointing, especially for phosphine-imidazol-2-ylidene ligands **121a-c**, which are structurally similar to the successful pyridyl-phosphinite ligands **105**. Improvement of the asymmetric induction could be possible by rigidifying the structure of both phosphine- and phosphinite-carbene ligands. A possible variation would be to incorporate a chiral cyclopentane in the chelate ring of either the phosphine- or phosphinite-NHC ligands as shown in Figure 4.16.

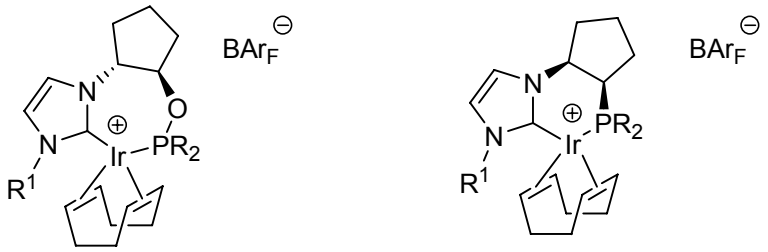


Figure 4.16 Possible rigidification of the phosphine- and phosphinite-NHC iridium complexes **121** and **131**.

4.6 Bibliography

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Chapter 5

Synopsis

5.1 Synopsis

The general objective of this research work was to investigate the potential of *N*-heterocyclic carbenes as ligands for the asymmetric iridium-catalysed hydrogenation of olefins and imines. In this context, efficient synthetic routes were developed to access three new classes of NHC-based ligands. The first class consists of chiral monodentate C_2-symmetric NHCs which are combined with two different co-ligands, pyridine or triphenylphosphine, in order to give rise to direct analogues of Crabtree's catalyst. In the second class, the NHC is tethered to a chiral oxazoline unit and forms a six-membered-chelate ring upon complexation. Finally, the third class of ligands consists of bidentate ligands, in which the NHC is linked to either a phosphine or a phosphinite moiety.

Analogues of Crabtree's catalyst bearing a chiral C_2-symmetric NHC

Six iridium complexes, analogues of Crabtree's catalyst bearing monodentate NHCs, were synthesised starting from readily available enantiopure C_2-symmetric imidazolium salts (Figure 5.1).

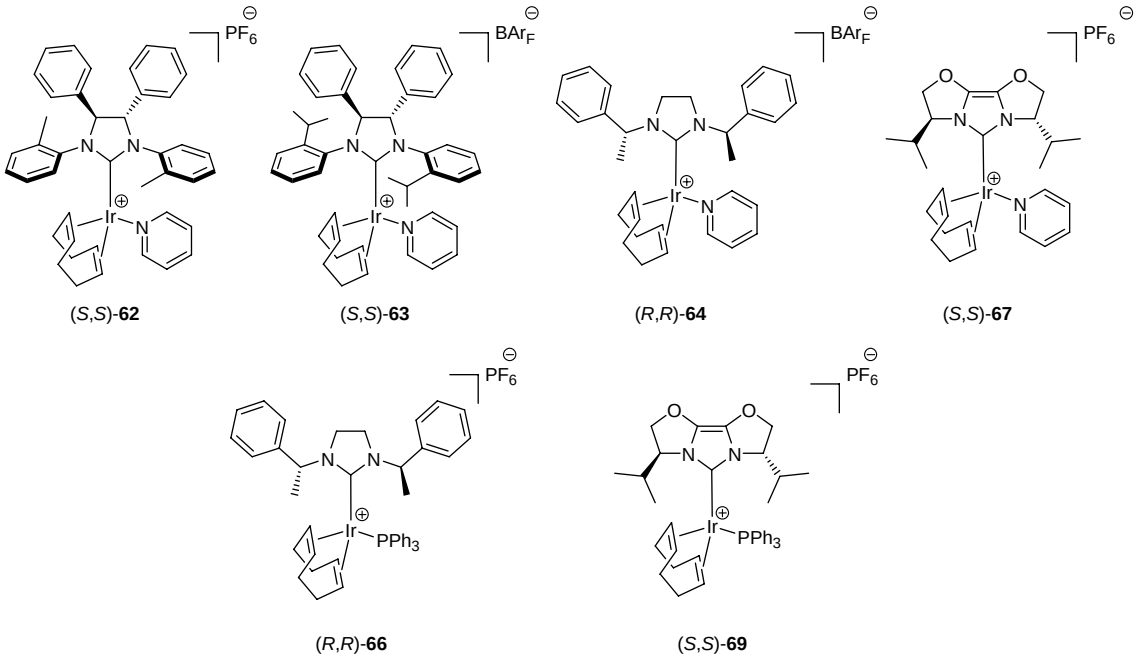


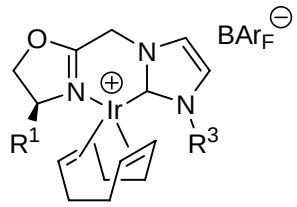
Figure 5.1 Analogues of Crabtree's catalyst.

Characterisation by crystallographic studies and 2D NMR gave insight into the geometry of the complexes and their dynamic behaviour. The catalytic activity of these new iridium complexes was tested in the enantioselective hydrogenation of a range of unfunctionalised

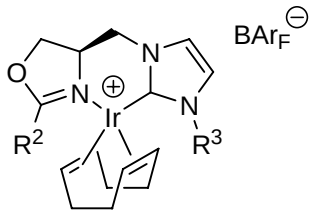
olefins. Full conversion of trisubstituted olefins was only obtained under forcing conditions (50 bar H_2, 100C°, 16h). Higher activities were measured for terminal olefin **73**, which was fully hydrogenated in 2 hours at room temperature and 50 bar H_2. The low enantioselectivities observed overall (up to 44%) are probably due to the lack of rigidity of such compounds compared to chelate complexes.

Oxazoline-NHC ligands

Two sets of oxazoline-NHC iridium complexes **81a-f** and **90a-o** were synthesised (Figure 5.2).



81a-f



90a-o

R^1 = ^{i}Pr, ^{t}Bu

R^2 = ^{t}Bu, 1-Ad, 2,6-$Me_2C_6H_3$

R^3 = Me, ^{i}Pr, ^{t}Bu, 2,4,6-$Me_3C_6H_2$, neopentyl, isobutyl

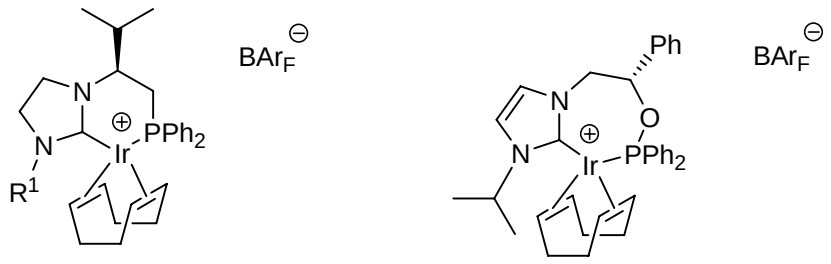
Figure 5.2 Oxazoline-NHC iridium complexes.

Simple and efficient syntheses, which enable easy variation of the ligand substituents, were developed for both classes. X-ray data analysis of one compound from each library confirmed that the electronic properties of the iridium are similar to those observed in Ir-P,N complexes. Complexes **81a-f** and **90a-o** were successfully tested in the asymmetric hydrogenation of unfunctionalised olefins. The high asymmetric inductions obtained (ee value up to 90% with *trans*-α-methylstilbene) were attributed to the rigidity generated by the six-membered chelate ring. Despite the wide range of catalysts investigated, the enantiomeric excesses measured with our two families did not compete with the most efficient Ir-P,N complexes.

Phosphine/phosphinite-NHC ligands

Three new iridium phosphine-NHC complexes **121a-c** (R^1 = Me, ^{i}Pr and mesityl) were synthesised and fully characterised by X-ray diffraction studies and 2D NMR analysis (Figure 5.3).

An efficient four step synthesis was developed from 2-phenyl oxirane, giving access to iridium complex **131**. The electronic properties of the two types of iridium complexes were investigated by X-ray analyses and NMR studies. In contrast to Ir-P,N and oxazoline-NHC complexes, almost no difference of the *trans* influence exerted on the two cod double bonds was observed.



121a-c **131**

Figure 5.3 Phosphine/phosphinite-NHC iridium complexes.

The four complexes were tested in the enantioselective hydrogenation of olefins. Low conversion values were measured in the hydrogenation of unfunctionalised olefins. However, promising activities (approximate TOF value of 400 h^{-1}) were found when functionalised substrates such as allylic alcohol and imines were hydrogenated. The moderate enantioselectivities measured throughout the screen are thought to originate from the lack of rigidity of the two types of complexes, which display conformers at room temperature as shown by 2D NMR analyses.

Chapter 6

Experimental

6.1 General aspects

6.1.1 Analytical techniques

TLC

Macherey-Nagel Polygram plates (40 x 80 mm) SIL G/UV_{254} (0.2 mm silica gel) with fluorescence indicator or ALOX/UV_{254} (0.2 mm aluminium oxide) were used for thin-layer chromatography.

Melting points

Melting points were measured with Büchi 535 melting point apparatus and are not corrected.

Optical rotation $[\alpha]_D^{20}$

Optical rotations were measured with a Perkin Elmer Polarimeter 341 (l = 1 dm, c in g/100 ml).

NMR spectra

NMR spectra were recorded on Bruker Avance 250, 400 and 500 MHz spectrometers equipped with BBO broadband. When needed the signal were assigned by 2D NMR experiments (APT, DEPT, COSY, HMQC, HMBC and NOESY).

For ^{1}H-NMR and ^{13}C-NMR spectra, solvent signals were used as internal reference:

^{1}H NMR: δ = 7.26 ppm ($CHCl_3$), δ = 5.32 ppm (CH_2Cl_2).

$^{13}C\{^{1}H\}$ NMR: δ = 77.1 ppm ($CHCl_3$), δ = 53.5 ppm (CH_2Cl_2).

For $^{31}P\{^{1}H\}$ NMR, the following external references were used:

Bruker Avance 250 and 400 MHz: H_3PO_4 = 0 ppm

Bruker Avance 500 MHz: $P{=}(PhO)_3$ = -18 ppm

IR

IR spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer. Spectra of liquids were measured as neat film between two NaCl plates; those of solids as KBr discs.

MS

EI and FAB mass spectra were recorded by Dr H. Nadig at the Department of Chemistry at the University of Basel on mass spectrometers VG70-250 (EI) and Finnigan MAT 312 (FAB), using 3-nitrobenzyl alcohol (3-NBA) as matrixes and sometimes KCl as additive in the latter case. The data are given in mass units per charge (m/e), and the intensities of the signals are indicated in percent of the basis ion.

Low resolution ESI (electrospray ionisation) mass spectra were measured by Dr Bruno Bulic, Dr Cara Humphrey, Dr Christian Markert and Antje Teichert with a Finnigan MAT LCQ octapole mass spectrometer.

EA

Elemental analyses were carried out by Mr Kirsch at the Department of Chemistry at the University of Basel on Leco CHN-900 (C-, H-, N-detection) and Leco RO-478 (O-detection) analysers. The data are indicated in mass percents.

GC

Carlo Erba HRGC Mega2 Series MFC 800 chromatographs were used. Achiral separation were mostly performed on the column Restek Rtx-1701, 0.25 μm, 30 m, 60 kPa He or H_2.

HPLC

For HPLC analysis, Shimadzu systems with a SCL-10A system controller, CTO-10AC column oven, LC10-AD pump system, DGU-14A degasser and a SPD-M10A diode array detector or a UV-vis detector (220 and 254 nm) were used. Chiral columns Chiracel OD-H, OB-H, OJ and Chiralpak AD from Daicel Chemical Industries Ltd. were used.

6.1.2 Working techniques and reagents

Reaction with air- or moisture-sensitive products were performed under Ar using standard Schlenk techniques or under purified N_2 in a MBraun glovebox (H_2O < 1 ppm, O_2 < 1 ppm). Glasware was oven dried and flame dried prior to use.

Diethyl ether, pentane and tetrahydrofuran were dried over potassium or sodium/benzophenone, dichloromethane over CaH_2 and freshly distilled under a stream of nitrogen prior to use. Other solvents were purchased dry at Fluka or Aldrich in septum sealed bottles and kept in an inert atmosphere over molecular sieves. When needed, solvents were degassed prior to use by three freeze-pump-thaw cycles.

Chromatography purifications were performed on silica gel (silica gel 60, Merck-Schuchardt, particle size 40-63 μm, 230-400 mesh) or alox (Aldrich, activated, basic Brockmann I, ~150 mesh, adjusted to grade III by adding 6% of water). Pressurised air or nitrogen were used to accelerate the purification.

General conditions for catalytic hydrogenation at elevated pressure

In a glove box, 0.1 mmol substrate, 1 mol% iridium complex and 0.5 ml CH_2Cl_2 were subsequently added to a 60 ml autoclave (Premex AG, Lengnau, Switzerland) with 4 glas inserts (1.5 ml) and magnetic stir bars. The autoclave was pressurised at 50 bar H_2 (Carbagas

Switzerland, 99.995%) and stirred for 2 hours. After pressure release, the solvent was evaporated and heptane (3 ml) was added. The resulting suspension was filtered through a short plug of silica gel eluting with mixture of hexane and Et_2O (typically 1:1) and the filtrate was analysed by GC and chiral HPLC to determine conversion and enantioselectivity (for analytical procedures and data, see J. Blankenstein and A. Pfaltz, *Angew. Chem., Int. Ed.* **2001**, *40*, 4445-4447.)

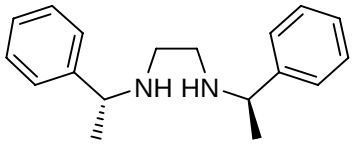
General conditions for catalytic hydrogenation at low pressure (1 bar H_2)

A solution of 0.1 mmol substrate with 1 mol% iridium complex in dry CH_2Cl_2 (2-3 ml) was prepared under inert atmosphere in a 20 ml Schlenk flask (Ø ~1.5 cm). The reaction mixture was stirred for ½-2 hours with slow bubbling of hydrogen gas through the solution, introduced through a stainless-steel needle. The temperature was kept constant at 25°C by a water bath. Work-up and analyses were performed as described for the hydrogenation at high pressure.

6.2 Analogues of Crabtree's catalyst bearing chiral C_2-symmetric NHC

6.2.1 Synthesis of diamines 48, 52a and 52b

(*R*,*R*)-*N*,*N*'-bis-(1-phenyl-ethyl)-ethane-1,2-diamine **48**



1,2-dichlorethane (10.21 g, 103 mmol) was added over 1 ½ hours to (*R*)-1-phenyl-ethylamine (25.0 g, 206 mmol) heated at 100°C. After 16 hours, the reaction mixture was cooled at 70°C and saturated aqueous KOH was added until the formation of two phases. The mixture was then extracted three times with CH_2Cl_2. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate an concentrated *in vacuo* to yield a yellow oil. The crude product was purified by distillation to yield a colourless oil (21.0 g, 78.3 mmol, 71%).

b.p. 140-142°C at 0.15 mbar;

$[\alpha]_D^{20}$ = + 66.9 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.36-7.20 (m, 10H; arom C*H*); 3.66 (q, ^3J(H,H) = 6.6 Hz, 2H; C*H*CH_3), 2.53 (mc, 4H; NCH_2), 1.79 (br, 2H; N*H*), 1.34 (d, ^3J(H,H) = 6.6 Hz, 6H; CHCH_3);

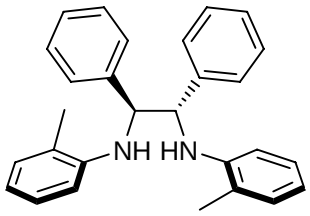
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 146.1 (2C; arom *C*), 128.8 (4C; arom *C*H), 127.2 (2C; arom *C*H), 127.0 (4C; arom *C*H), 58.6 (2C; *C*HCH_3), 47.6 (2C; NCH_2), 24.8 (2C; CHCH_3);

IR (NaCl): $\tilde{\nu}$ = 2962m, 2875w, 1598w, 1495w, 1464w, 1358m, 1189m, 1177s, 1097w, 1019w, 993w, 940m, 884m, 816m, 786w, 730w, 664m cm^{-1};

MS (FAB): *m/z* (%): 269 (56) $[M + H]^+$, 105 (100);

EA calcd (%) for $C_8H_{16}ClNO_2$ (268.40): C 80.55, H 9.01, N 10.44; found: C 79.89, H 8.98, N 10.56.

(*S*,*S*)-1,2-diphenyl-*N*,*N*'-di-o-tolyl-ethane-1,2-diamine **52a**



A solution of $Pd(OAc)_2$ (52 mg, 0.231 mmol), (±)BINAP (288 mg, 0.463 mmol), NaO*t*Bu (1.36 g, 14.15 mmol) in toluene (80 ml) was stirred at room temperature. After 20 minutes, (*S*,*S*)-diphenylethylenediamine (1.00 g, 4.71 mmol) and 1-bromo-2-methyl-benzene (1.69 g, 9.90 mmol) were added to the mixture. The reaction mixture was stirred at 100°C for 16 hours then concentrated *in vacuo* to remove the toluene. The crude oil was purified by chromatography on silica gel eluting with a mixture of ethyl acetate and hexane (1:9) to yield a white solid (1.52 g, 3.86 mmol, 82%). If an oil is obtained at the end of the chromatography, trituration of the crude product in hexane produces white crystal.

$\boldsymbol{R_f}$ = 0.50 (EtOAc/Hexane 1:9);

m.p. 111-112°C (hexane);

$[\alpha]_D^{20}$ = -153.1 (c = 0.50, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.32-7.22 (m, 10H; arom C*H*), 7.04 (d, *J*(H,H) = 7.3 Hz, 2H; arom C*H*), 6.92 (t, *J*(H,H) = 7.7 Hz, 2H; arom C*H*), 6.63 (t, *J*(H,H) = 7.4 Hz, 2H; arom C*H*), 6.31 (d, *J*(H,H) = 8.1 Hz, 2H; arom C*H*), 4.74 (s, 2H; NHC*H*), 4.52 (br, 2H; N*H*), 2.17 (s, 6H; arom CH_3);

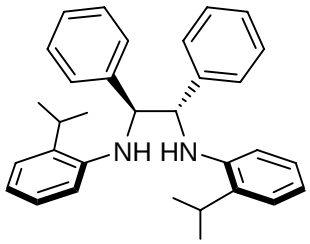
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 145.4 (2C; arom *C*H), 140.4 (2C; arom *C*H), 130.4 (2C; arom *C*H), 129.1 (4C; arom *C*H), 128.1 (2C; arom *C*H), 127.6 (4C; arom *C*H), 127.3 (2C; arom *C*H), 123.3 (2C; arom *C*H), 118.1 (2C; arom *C*H), 112.2 (2C; arom *C*H), 64.3 (2C; NH*C*H), 18.0 (2C; *C*H_3);

IR (KBr): $\tilde{\nu}$ = 3411m, 3023m, 2918w, 2852m, 1606m, 1588m, 1508s, 1481m, 1450m, 1346m, 1312m, 1264m, 1200w, 1130m, 1070w, 1051m, 1030w, 986w, 758m, 745s, 699s, 518w, 442w cm^{-1};

MS (FAB): *m/z* (%): 393 (4) $[M + H]^+$, 196 (100);

EA calcd (%) for $C_{28}H_{28}N_2$ (392.55): C 85.67, H 7.19, N 7.14; found: C 85.51, H 6.95, N 7.11.

(*S*,*S*)-*N*,*N*'-bis-(2-isopropyl-phenyl)-1,2-diphenyl-ethane-1,2-diamine **52b**



A solution of $Pd(OAc)_2$ (52 mg, 0.231 mmol), (±)BINAP (288 mg, 0.463 mmol), NaO*t*Bu (1.36 g, 14.15 mmol) in toluene (80 ml) was stirred at room temperature. After 20 minutes, (*S*,*S*)-diphenylethylenediamine (1.00 g, 4.71 mmol) and 1-bromo-2-isopropyl-benzene (1.97 g, 9.90 mmol) were added to the mixture, which was subsequently stirred at 100°C for 14 hours. Hexane (100 ml) was added to the cooled mixture. Filtration through a plug of silica gel followed by concentration *in vacuo* gave a yellow oil, which was triturated in hexane to yield as a white solid (1.86 g, 4.14 mmol, 88%).

R_f = 0.56 (EtOAc/Hexane 1:9);

m.p. 85-86°C (hexane);

$[\alpha]_D^{20}$ = -141.8 (c = 0.39, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.35-7.20 (m, 10H; arom C*H*), 7.11 (d, *J*(H,H) = 7.6 Hz, 2H; arom C*H*), 6.89 (t, *J*(H,H) = 7.5 Hz, 2H; arom C*H*), 6.69 (t, *J*(H,H) = 7.4 Hz, 2H; arom C*H*), 6.30 (d, *J*(H,H) = 8.1 Hz, 2H; arom C*H*), 4.75 (s, 2H; NHC*H*), 4.66 (br, 2H; N*H*), 2.89 (hept, ^3J(H,H) = 6.8 Hz, 2H; C*H*$(CH_3)_2$), 1.30 (d, ^3J(H,H) = 6.8 Hz, 6H; CH(C*H*$_3)_2$), 1.16 (d, ^3J(H,H) = 6.8 Hz, 6H; CH(C*H*$_3)_2$);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 143.9 (2C; arom *C*H), 140.5 (2C; arom *C*H), 133.6 (2C; arom *C*H), 129.1 (4C; arom *C*H), 128.1 (2C; arom *C*H), 127.5 (4C; arom *C*H), 126.8 (2C; arom *C*H), 125.3 (2C; arom *C*H), 118.3 (2C; arom *C*H), 112.9 (2C; arom *C*H), 64.3 (2C; NH*C*H), 27.8 (2C; *C*H$(CH_3)_2$), 22.9 (CH(*C*H$_3)_2$), 22.7 (CH(*C*H$_3)_2$);

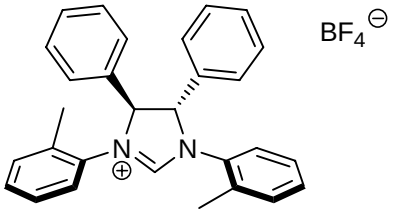
IR (KBr): $\tilde{\nu}$ = 3413w, 3061w, 3027w, 2960m, 2868m, 1603m, 1584m, 1505s, 1451m, 1356w, 1301m, 1278m, 1258m, 1119w, 1078w, 927w, 893w, 774w, 744m, 700m, 521w cm^{-1};

MS (FAB): *m/z* (%): 449 (4) $[M + H]^+$, 224 (100);

EA calcd (%) for $C_{32}H_{36}N_2$ (448.65): C 85.67, H 8.09, N 6.24; found: C 85.42, H 8.11, N 6.04.

6.2.2 Synthesis of imidazolium salts 53a and 53b and 49

(*S*,*S*)-[4,5-diphenyl-1,3-di-*o*-tolyl-4,5-dihydro-3*H*-imidazol-1-ium]-tetrafluoroborate **53a**



A solution of diamine **52a** (300 mg, 0.764 mmol) and NH_4BF_4 (84 mg, 0.80 mmol) in triethylorthoformate (1.0 ml, 6.5 mmol) was heated at 110°C for 5 hours. The crude oil was decanted and precipitation occurred upon addition of Et_2O. The white solid was washed three times with Et_2O and dissolved in CH_2Cl_2 (5 ml). The organic layer was filtered and concentrated *in vacuo* to yield a white solid (371mg, 0.756 mmol, 99%).

m.p. 114-116°C;

$[\alpha]_D^{20}$ = -381 (c = 0.10, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 8.27 (s, NC*H*N), 7.45-7.32 (m, 12H; arom C*H*), 7.22-7.09 (m, 6H; arom C*H*), 5.77 (s, 2H; NHC*H*), 2.44 (s, 6H; CH_3);

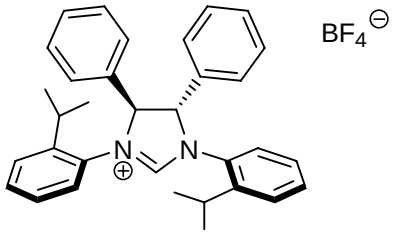
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 157.9 (N*C*HN), 133.92 (2C), 133.90 (2C), 133.1 (2C), 132.1 (2C), 130.8 (2C), 130.5 (2C), 130.1 (4C), 128.6 (4C), 128.2 (2C), 128.1 (2C), 76.6 (2C; NH*C*H), 18.0 (2C; *C*H_3);

IR (KBr): $\tilde{\nu}$ = 3063w, 1619s, 1600s, 1578m, 1495m, 1457m, 1269m, 1213m, 1190m, 1059brs, 885w, 822w, 764m, 700m, 633w, 583w, 546w, 521w, 456w cm^{-1};

MS (FAB): *m/z* (%): 403 (100) $[M - BF_4]^+$;

EA calcd (%) for $C_{29}H_{27}BF_4N_2$ (490.34): C 71.04, H 5.55, N 5.71; found: C 70.58, H 5.51, N 5.78.

(*S*,*S*)-[1,3-bis-(2-isopropyl-phenyl)-4,5-diphenyl-4,5-dihydro-3*H*-imidazol-1-ium]-tetrafluoroborate **53b**



Synthesis according to the previous general procedure using diamine **52b** (902 mg, 2.01 mmol), NH_4BF_4 (253 mg, 2.41 mmol) and triethylorthoformate (2.5 ml) yielded an amorphous white hygroscopic solid (1066 mg, 1.95 mmol, 97%).

m.p. not measurable due to the product hygroscopicity;

$[\alpha]_D^{20}$ = -94.2 (c = 0.20, $CHCl_3$);

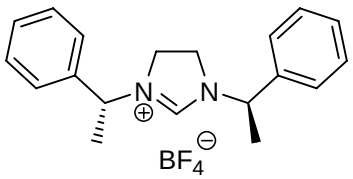
^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 8.27 (s, 1H; NC*H*N), 7.53 (mc, 2H; arom C*H*), 7.48-7.28 (m, 14H; arom C*H*), 7.19 (mc, 2H; arom C*H*), 5.80 (s, 2H; NHC*H*), 3.12 (hept, ^3J = 6.8 Hz, 2H; C*H*(CH_3)$_2$), 1.32 (d, ^3J(H,H) = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 1.17 (d, ^3J(H,H) = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 157.8 (N*C*HN), 145.2 (2C; arom), 133.2 (2C; arom), 131.3 (br, 4C; arom), 130.9 (2C; arom), 130.1 (4C; arom), 129.0 (4C; arom), 128.6 (2C; arom), 128.1 (2C; arom), 127.4 (2C; arom), 29.0 (2C; *C*H(CH_3)$_2$), 25.0 (2C; CH(*C*H$_3$)$_2$), 24.4 (2C; CH(*C*H$_3$)$_2$), 2C N*C*HCHN under the CH_3Cl signal;

IR (KBr): $\tilde{\nu}$ = 3367w, 3282w, 3065w, 2967m, 2931w, 2872w, 1710w, 1619s, 1600m, 1576m, 1491m, 1457m, 1389w, 1367w, 1276m, 1228m, 1213m, 1183w, 1059sbr, 877w, 761m, 700m, 634w, 572w, 521m cm^{-1};

MS (FAB): *m/z* (%): 459 (100) $[M - BF_4]^+$.

(*R*,*R*)-[1,3-bis-(1-phenyl-ethyl)-4,5-dihydro-3*H*-imidazol-1-ium]-tetrafluoroborate **49**



Synthesis according to the previous general procedure using diamine **48** (2.00 g, 7.45 mmol), NH_4BF_4 (937 mg, 8.94 mmol) and triethylorthoformate (6.5 ml) yielded a white solid (2.54 g, 6.93 mmol, 97%).

m.p. 115-116°C;

$[\alpha]_D^{20}$ = -18.1 (c = 0.50, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 8.44 (s, 1H; NC*H*N), 7.41-7.28 (m, 10H; arom C*H*), 4.95 (q, ^3J(H,H) = 6.9 Hz, 2H; C*H*CH_3), 3.68 (mc, 4H; NCH_2), 1.74 (d, ^3J(H,H) = 6.9 Hz, 6H; CHCH_3);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 155.1 (N*C*HN), 137.9 (2C; arom *C*), 129.7 (4C; arom *C*H), 129.3 (2C; arom *C*H), 127.4 (4C; arom *C*H), 58.6 (2C; N*C*H), 46.7 (2C; N*C*H_2), 19.3 (2C; *C*H_3)

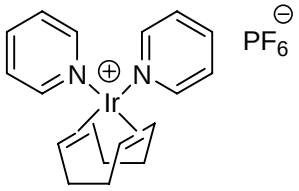
IR (KBr): $\tilde{\nu}$ = 3112w, 3031w, 2982w, 2943w, 2898w, 1638s, 1509w, 1495w, 1455m, 1355w, 1330w, 1303w, 1269m, 1199m, 1127m, 1044s, 774m, 708m, 638w, 604w, 586w, 542w, 521w, 507w, 464w cm^{-1};

MS (FAB): *m/z* (%): 279 (100) $[M - BF_4]^+$;

EA calcd (%) for $C_{19}H_{23}N_2BF_4$ (366.21): C 62.32, H 6.33, N 7.65; found: C 62.31, H 6.26, N 7.55.

6.2.3 Synthesis of iridium precursors 58a and 58b

(η^4-1,5-cyclooctadiene**)**bis(pyridine)iridium(I)-hexafluorophosphate **58a**



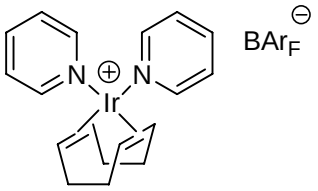
A solution of [(η^4-cod)IrCl]$_2$ (420 mg, 0.625 mmol), pyridine (0.7 ml, 8.7 mmol) and NH_4PF_6 (310 mg, 1.90 mmol) in a degassed acetone water mixture (1:1, 20 ml) was stirred under argon at room temperature for 12 hours, or until the red solid has dissolved. The solution was concentrated *in vacuo* until the volume of the mixture was reduced to approximately 10 ml. The precipitate was filtered and washed with three portions (5 ml) of degassed water to yield a yellow crystalline solid (732 mg, 1.21 mmol, 97%).

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 8.72 (mc, 4H; arom C*H*), 7.72 (mc, 2H; arom C*H*), 7.48 (mc, 4H; arom C*H*), 3.83 (mc, 4H; cod C*H*), 2.47 (mc, 4H; cod CH_2), 1.82 (mc, 4H; cod CH_2);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 150.1 (4C; arom *C*H), 139.1 (2C; arom *C*H), 127.3 (4C; arom *C*H), 71.2 (4C; cod *C*H), 31.4 (8C; cod *C*H);

IR (KBr): $\tilde{\nu}$ = 3111w, 2980w, 2919w, 2890w, 2839w, 1605w, 1483w, 1449w, 1331w, 1214w, 1158w, 1069w, 1006w, 835wbr, 762m, 698m, 556m, 493w;
MS (FAB): *m/z* (%):459 (100) $[M - PF_6]^+$, 380 $[M - PF_6 - pyridine]^+$,
EA calcd (%) for $C_{18}H_{22}F_6IrN_2P$ (603.55): C 35.82, H 3.67, N 4.64; found: C 35.90, H 3.52, N 4.50.

(η^4-1,5-cyclooctadiene**)**bis(pyridine)iridium(I)-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **58b**.

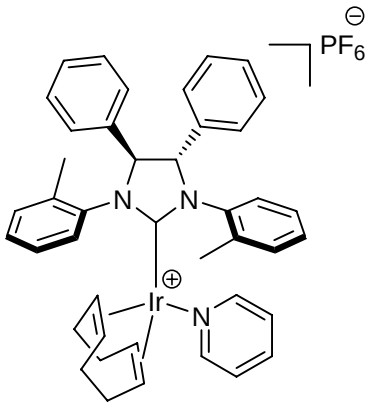


A solution of $[(\eta^4\text{-cod})IrCl]_2$ (420 mg, 0.625 mmol), pyridine (0.7 ml, 8.7 mmol) and $NaBAr_F$ (1.683 g, 1.90 mmol) in CH_2Cl_2 (20 ml) was stirred under argon at room temperature for 12 hours. The solution was filtered and concentrated *in vacuo* to yield a yellow crystalline solid (1.566 mg, 1.18 mmol, 95%).

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 8.45 (mc, 4H; arom C*H*), 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.61 (mc, 2H; arom C*H*), 7.50 (mc, 4H; BAr_F *para* C*H*), 7.30 (mc, 4H; arom C*H*), 3.81 (mc, 4H; cod C*H*), 2.39 (mc, 4H; cod CH_2), 1.86 (mc, 4H; cod CH_2);
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 162.0 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 149.4 (4C; arom *C*H), 139.6 (2C; arom *C*H), 135.2 (br, 8C; BAr_F *ortho C*H), 129.4 (q, ^2J(F,C) = 31.1 Hz, 8C; BAr_F *C ipso* to CF_3), 127.4 (4C; arom *C*H), 124.9 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 117.5 (br, 4C; BAr_F *para C*H), 72.0 (4C; cod *C*H), 31.6 (8C; cod *C*H);
IR (KBr): $\tilde{\nu}$ = 3182w, 3069w, 2977w, 2889w, 2841w, 1611w, 1438m, 1357s, 1279s, 1127s, 935w, 889m, 840w, 779w, 745w, 709m, 676m, 542w;
MS (FAB): *m/z* (%): 459 (45) $[M - BAr_F]^+$, 380 $[M - BAr_F - pyridine]^+$,
EA calcd (%) for $C_{50}H_{34}BF_{24}IrN_2$ (1321.79): C 45.43, H 2.59, N 2.12; found: C 45.58, H 2.41, N 2.20.

6.2.4 Synthesis of iridium complexes 62-69

(*S*,*S*)-[**(**η^4-1,5-cyclooctadiene**)**-(4,5-diphenyl-1,3-di-*o*-tolyl-imidazol-2-ylidene)-(pyridine)iridium(I)]-hexafluorophosphate **62**.



Schwesinger base BEMP (224 mg, 0.816 mmol) was added to a solution of iridium complex **58a** (492 mg, 0.816 mmol) and imidazolium salt **53a** (400 mg, 0.816 mmol) in CH_2Cl_2 (20 ml). The reaction was stirred at room temperature for 6 hours then concentrated *in vacuo* to remove CH_2Cl_2. The crude product was purified by chromatography on silica gel eluting with 1% methanol in CH_2Cl_2 to yield a yellow solid. The complex was crystallised from a mixture of Et_2O and CH_2Cl_2 to yield a yellow crystalline solid (393 mg, 0.424 mmol, 52%). Single crystals suitable for X-ray diffraction analysis were obtained by layering a saturated solution of the complex in CH_2Cl_2 with Et_2O.

$[\alpha]_D^{20}$ = -250 (c = 0.287, CH_2Cl_2);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.92 (mc, 1H; pyr C*H*), 7.82 (mc, 2H; pyr C*H*), 7.71 (mc, 1H; arom C*H*), 7.56 (mc, 1H; arom C*H*), 7.50-7.25 (m, 13H; 11 x arom C*H*, 2 x pyr C*H*), 7.23-7.13 (m, 3H; arom C*H*), 7.06 (mc, 2H; arom C*H*), 5.4 (d, ^3J(H,H) = 5.5 Hz, 1H; NC*H*), 5.15 (d, ^3J(H,H) = 5.3 Hz, 1H; NC*H*), 4.16 (mc, 1H; cod C*H*), 3.74 (mc, 1H; cod C*H*), 3.19 (mc, 2H; cod C*H*), 2.42 (s, 3H; CH_3), 2.37 (mc, 1H; cod CH_2), 2.01 (mc, 2H; cod CH_2), 1.85 (mc, 1H; cod CH_2), 1.69 (mc, 4H; 3 x CH_3 + 1 x cod CH_2), 1.55 (mc, 1H; cod CH_2), 1.42 (mc, 1H; cod CH_2), 1.29 (mc, 1H; cod CH_2); two conformers present in a 100:7 ratio, only the major conformer is described;

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 202.7 (N*C*N), 151.1 (2C, pyr *C*H), 139.1 (C, pyr *C*H), 138.5 (arom *C*), 138.4 (arom *C*), 137.9 (arom *C*), 137.8 (arom *C*), 135.9 (arom *C*), 134.1 (arom *C*), 132.5 (arom *C*H), 132.4 (arom *C*H), 131.4 (br, 2C; arom *C*H), 130.1 (br, arom *C*H), 130.0 (br, arom *C*H), 129.5 (br, arom *C*H), 127.3 (br, arom *C*H), 127.1 (br, arom

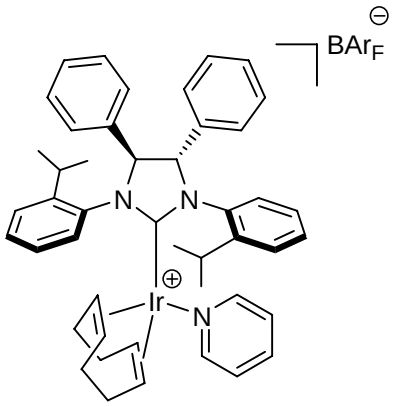
*C*H), 127.0 (2C; pyr *C*H), 85.6 (cod *C*H), 84.0 (cod *C*H), 76.5 (N*C*H), 76.3 (N*C*H), 65.5 (cod *C*H), 65.1 (cod *C*H), 33.7 (cod *C*H_2), 31.3 (cod *C*H_2), 30.5 (cod *C*H_2), 28.5 (cod *C*H_2), 19.8 (*C*H_3), 18.6 (*C*H_3);

IR (KBr): $\tilde{\nu}$ = 3028w, 2948w, 2882w, 2834w, 1605w, 1491m, 1458m, 1413m, 1390m, 1341w, 1309m, 1268m, 1236m, 1217m, 1199m, 1159w, 1115w, 1003w, 952w, 850s, 828s, 759m, 720m, 700m, 650w, 610w, 557m, 518w, 461w cm^{-1};

MS (FAB): *m/z* (%): 782 (28) $[M - PF_6]^+$, 701 (100), 591 (23);

EA calcd (%) for $C_{42}H_{43}F_6N_3PIr \cdot ½CH_2Cl_2$ (969.46): C 52.65, H 4.57, N 4.33; found: C 52.94, H 4.50, N 4.21.

(*S*,*S*)-[**(**η^4-1,5-cyclooctadiene**)-**[1,3-bis-(2-isopropyl-phenyl)-4,5-diphenyl-imidazol-2-ylidene]-(pyridine)iridium(I)]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **63**



Schwesinger base BEMP (151 mg, 0.549 mmol) was added to a solution of iridium complex **58b** (726 mg, 0.549 mmol) and imidazolium salt **53b** (300 mg, 0.549 mmol) in toluene (14 ml). The reaction was stirred at room temperature for 4 hours then concentrated *in vacuo* to remove toluene. The crude product was purified by chromatography on silica gel eluting with a mixture of CH_2Cl_2 and pentane (1:1) to yield a yellow solid. The complex was crystallised from a mixture of Et_2O and pentane to yield a yellow crystalline product (289 mg, 0.170 mmol, 31%).

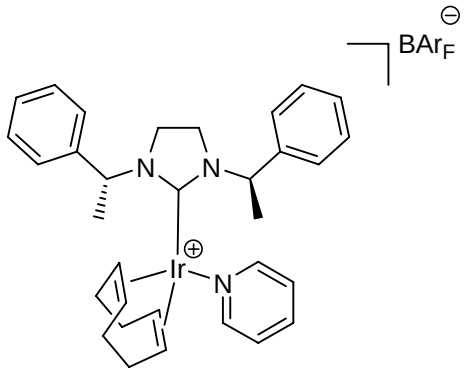
$[\alpha]_D^{20}$ = +138 (c = 0.237, $CHCl_3$);

IR (KBr): $\tilde{\nu}$ = 3038w, 2968w, 2930w, 2890w, 2843w, 1609w, 1488m, 1458m, 1413m, 1355s, 1277s, 1127s, 898m, 887m, 839m, 756w, 711m, 698m, 682m, 869m, 542w cm^{-1};

MS (FAB): *m/z* (%): 838 (19) $[M - BAr_F]^+$, 757 (100), 647 (49);

EA calcd (%) for $C_{78}H_{63}BF_{24}IrN_3$ (1701.36): C 55.07, H 3.73, N 2.47; found: C 55.04, H 3.60, N 2.33.

(*R*,*R*)-[**(**η^4-1,5-cyclooctadiene**)**-[1,3-bis-(1-phenyl-ethyl)-imidazol-2-ylidene]-(pyridine)iridium(I)]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **64**.



Schwesinger base BEMP (137 mg, 0.500 mmol) was added to a solution of iridium complex **58b** (661 mg, 0.500 mmol) and imidazolium salt **49** (183 mg, 0.549 mmol) in toluene (12 ml). The reaction was stirred at room temperature for 4 hours then concentrated *in vacuo* to remove toluene. The crude product was purified by chromatography on silica gel eluting with a mixture of CH_2Cl_2 and pentane (1:1) to yield a yellow crystalline solid. (236 mg, 0.155 mmol, 31%).

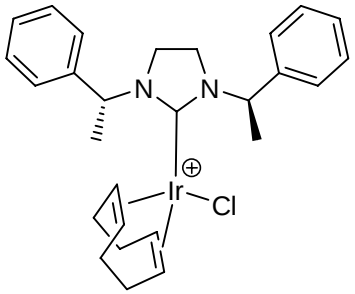
$[\alpha]_D^{20}$ = -26 (c = 0.146, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.13 (mc, 2H; pyr C*H*), 7.71 (mc, 8H; BAr_F *ortho* C*H*), 7.52 (mc, 5H; 4 x BAr_F *para* C*H* + 1 x pyr C*H*), 7.46-7.33 (m, 3H; arom C*H*), 7.31-7.18 (m, 5H; arom C*H*), 7.05 (mc, 2H; pyr C*H*), 6.90 (mc, 2H; arom C*H*), 6.50 (q, ^3J(H,H) = 6.9 Hz, 2H; C*H*CH_3), 6.43 (q, ^3J(H,H) = 7.0 Hz, 1H; C*H*CH_3), 3.83-3.77 (m, 2H; cod C*H*), 3.76-3.67 (m, 2H; cod C*H*), 3.65-3.48 (m, 4H; NCH_2), 2.40-2.25 (m, 3H; cod CH_2), 2.08-1.97 (m, 2H; cod CH_2), 1.93 (mc, 1H; cod CH_2), 1.82-1.65 (m, 5H; 2 x cod CH_2 + 3 x CHC*H*$_3$), 1.49 (d, ^3J(H,H) = 7.1 Hz, 3H; CHC*H*$_3$);

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 203.7 (N*C*N), 161.8 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 150.5 (2C, pyr *C*H), 140.3 (arom *C*), 139.4 (arom *C*), 138.3 (pyr *C*H), 134.9 (br, 8C; BAr_F *ortho C*H), 129.4 (2C; arom *C*H), 129.3 (2C; arom *C*H), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 128.5 (arom *C*H), 128.2 (arom *C*H), 126.6 (2C; pyr *C*H), 126.0 (2C; arom *C*H), 125.2 (2C; arom C*H*), 124.6 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 117.6 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F *para C*H), 85.1 (cod *C*H), 84.7 (cod *C*H), 65.6 (cod *C*H), 65.4 (cod *C*H), 58.3 (*C*HCH$_3$), 58.0 (*C*HCH$_3$), 44.2 (N*C*H$_2$), 43.9 (N*C*H$_2$), 33.1 (cod *C*H$_2$), 31.8 (cod *C*H$_2$), 30.2 (cod *C*H$_2$), 29.2 (cod *C*H$_2$), 19.68 (N*C*H$_3$), 19.63 (N*C*H$_3$);

IR (KBr): $\tilde{\nu}$ = 2925w, 1609w, 1487m, 1449m, 1355s, 1275s, 1124s, 931w, 885m, 839m, 753w, 714m, 698m, 681m, 669m cm^{-1};
MS (FAB): *m/z* (%): 658 (11) $[M - BAr_F]^+$, 579 (100) $[M - BAr_F - pyridine]^+$, 469 (93);
EA calcd (%) for $C_{64}H_{51}BF_{24}IrN_3$ (1521.11): C 50.54, H 3.38, N 2.76; found: C 50.56, H 3.31, N 2.70.

(*R*,*R*)-[**(**η^4-1,5-cyclooctadiene**)**-[1,3-bis-(1-phenyl-ethyl)-imidazol-2-ylidene]iridium(I)]-chloride **65**.



Schwesinger base BEMP (100 mg, 0.366 mmol) was added to a solution of $[(\eta^4\text{-cod})IrCl]_2$ (123 mg, 0.184 mmol) and imidazolium salt **49** (200 mg, 0.366 mmol) in THF (10 ml). The reaction was stirred at room temperature for 6 hours then concentrated *in vacuo* to remove THF. The crude product was purified by chromatography on silica gel eluting with a mixture of ethyl acetate and hexane (1:10) to yield a yellow solid (157 mg, 0.256 mmol, 70%). Single crystals suitable for X-ray diffraction analysis were obtained by layering a saturated solution of the complex in CH_2Cl_2 with pentane.

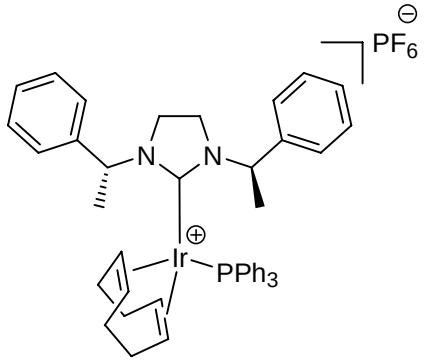
$[\alpha]_D^{20}$ = +34 (c = 0.139, $CHCl_3$);
^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.71 (mc, 2H; arom C*H*), 7.42-7.34 (m, 6H; arom C*H*), 7.34-7.26 (m, 2H; arom C*H*), 6.55 (q, ^3J(H,H) = 7.0 Hz, 1H; C*H*CH_3), 6.45 (q, ^3J(H,H) = 7.0 Hz, 1H; C*H*CH_3), 4.60 (mc, 2H; cod C*H*), 3.38 (mc, 2H; NCH_2), 3.29-3.15 (m, 3H; 2 x cod C*H* + 1 x NCH_2), 3.08 (mc, 1H; NCH_2), 2.32-2.04 (m, 4H; cod CH_2), 1.80-1.65 (m, 9H; 6 x CH_3 + 3 x cod CH_2), 1.55 (mc, 1H; cod CH_2);
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 205.8 (N*C*N), 141.1 (arom *C*), 139.4 (arom *C*), 128.7 (2C; arom *C*H), 128.5 (2C; arom *C*H), 127.8 (2C; arom *C*H), 127.6 (arom *C*H), 127.4 (arom *C*H), 127.0 (2C; arom *C*H), 85.1 (cod *C*H), 85.0 (cod C*H*), 57.6 (C*H*CH_3), 56.6 (C*H*CH_3), 52.4 (cod *C*H), 51.7 (cod *C*H), 43.3 (N*C*H_2), 42.7 (N*C*H_2), 33.7 (cod *C*H_2), 33.2 (cod *C*H_2), 29.3 (cod *C*H_2), 29.1 (cod *C*H_2), 17.6 (*C*H_3), 17.4 (*C*H_3);

IR (KBr): $\tilde{\nu}$ = 2976m, 2933m, 2867m, 2834m, 1484m, 1443s, 1374m, 1321m, 1295m, 1265s, 1213m, 1187m, 1153m, 1070w, 1025m, 966w, 863w, 786m, 756m, 702m, 649w, 640m, 624w, 517w, 458w cm^{-1};

MS (FAB): *m/z* (%): 614 (100), 579 (49) $[M - Cl]^+$, 470 (75);

EA calcd (%) for $C_{27}H_{34}ClIrN_2$ (614.26): C 52.580, H 5.58, N 4.56; found: C 52.65, H 5.49, N 4.34.

(*R*,*R*)-[**(**η^4-1,5-cyclooctadiene**)**-[1,3-bis-(1-phenyl-ethyl)-imidazol-2-ylidene]-(triphenylphosphine)iridium(I)]-hexafluorophosphate **66**.



A solution of $AgPF_6$ (61 mg, 0.244 mmol) in THF (2 ml) was added to a solution of iridium complex **65** (150 mg, 0.244 mmol) in a mixture of CH_2Cl_2 and THF (1:1, 2 ml). The mixture was stirred at room temperature for 10 minutes then filtered to remove silver chloride. A solution of PPh_3 (64 mg, 0.244 mmol) in THF (2 ml) was added to the filtrate. The reaction mixture was stirred at room temperature for 30 minutes and was concentrated *in vacuo* to give a red solid. The crude product was purified by chromatography on silica gel eluting with 1% MeOH in CH_2Cl_2. The complex was crytallised by layering a saturated solution of the complex in CH_2Cl_2 with Et_2O (219 mg, 0.222 mmol, 91%).

$[\alpha]_D^{20}$ = +13 (c = 0.151, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.51-7.45 (m, 3H; arom C*H*), 7.44-7.34 (m, 8H; arom C*H*), 7.32-7.21 (m, 7H; arom C*H*), 7.20-7.12 (m, 3H; arom C*H*), 7.11-7.04 (m, 3H; arom C*H*), 5.99 (q, ^3J(H,H) = 7.1 Hz, 1H; C*H*CH_3), 5.51 (q, ^3J(H,H) = 7.2 Hz, 1H; C*H*CH_3), 4.36 (mc, 2H; cod C*H*), 4.11 (mc, 1H; NCH_2), 4.00 (mc, 1H; cod C*H*), 3.86 (mc, 2H; NCH_2), 3.53 (mc, 1H; cod C*H*), 3.34 (mc, 1H; NCH_2), 2.42-2.23 (m, 2H; cod CH_2), 2.04 (mc, 1H; cod CH_2), 1.92 (mc, 2H; cod CH_2), 1.75 (d, ^3J(H,H) = 7.1 Hz, 3H; CH_3), 1.72-1.51 (m, 3H; cod CH_2), 0.56 (d, ^3J(H,H) = 7.1 Hz, 3H; CH_3);

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 202.7 (d, ^{2}J(P,C) = 8.0 Hz; N*C*N), 142.2 (arom *C*), 139.0 (arom *C*), 134.0, 133.9, 131.61, 131.59, 130.7 (arom *C*), 130.3 (arom *C*), 129.3, 129.0, 128.9, 128.8, 128.1, 127.7, 127.3, 125.1, 88.1 (d, ^{2}J(P,C) = 8.5 Hz; cod *C*H), 82.9 (d, ^{2}J(P,C) = 13.2 Hz; cod *C*H), 81.3 (cod *C*H), 78.3 (cod *C*H), 60.4 (*C*HCH$_3$), 58.7 (*C*HCH$_3$), 45.6 (N*C*H$_2$), 44.8 (N*C*H$_2$), 32.34 (br, cod *C*H$_2$), 32.27 (br, cod *C*H$_2$), 29.7 (br, cod *C*H$_2$), 28.6 (br, cod *C*H$_2$), 20.2 (*C*H$_3$), 19.5 (*C*H$_3$);

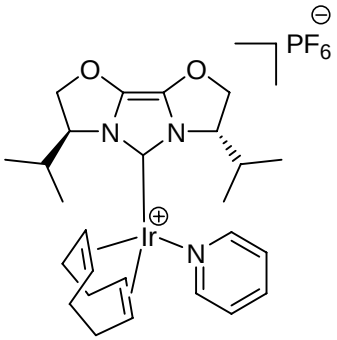
^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 295 K) : δ = 16.9 (s);

IR (KBr): $\tilde{\nu}$ = 3056w, 2964w, 2885w, 2834w, 1481m, 1435m, 1327w, 1264m, 1208w, 1149w, 1092m, 1024w, 999w, 837s, 783w, 750m, 636w, 612w, 558m, 532m, 511m, 493w, 454w, 421w cm^{-1};

MS (FAB): *m/z* (%): 841 (100) [M – BAr_F]$^{+}$, 577 (20), 471 (68) [M – BAr_F – PPh_3]$^{+}$;

EA calcd (%) for $C_{45}H_{49}F_6IrN_2P_2$ (986.06): C 54.81, H 5.01, N 2.84; found: C 54.70, H 4.87, N 2.70.

(*S*,*S*)-[**(**η^{4}-1,5-cyclooctadiene**)**-(isopropyl-bioxazolin-ylidene)-(pyridine)iridium(I)]-hexafluorophosphate **67**.



Schwesinger base BEMP (142 mg, 0.517 mmol) was added to a solution of iridium complex **58a** (312 mg, 0.517 mmol) and imidazolium salt **55** (200 mg, 0.517 mmol) in CH_2Cl_2 (20 ml). The reaction was stirred at room temperature for 6 hours then concentrated *in vacuo* to remove CH_2Cl_2. The crude product was purified by chromatography on silica gel eluting with a mixture of CH_2Cl_2 and pentane (2:1), CH_2Cl_2 and 1% methanol in CH_2Cl_2 to yield a yellow solid. The complex was crystallised from a mixture of pentane and CH_2Cl_2 to yield a yellow crystalline product (338 mg, 0.445 mmol, 86%).

$[\alpha]_D^{20}$ = -42.2 (c = 0.50, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.53 (mc, 2H; pyr C*H*), 7.89 (mc, 1H; pyr C*H*), 7.57 (mc, 2H; pyr C*H*), 4.89 (mc, 1H; oxaz C*H*$_2$), 4.75 (mc, 1H; oxaz C*H*$_2$), 4.71-4.62 (m, 3H; 1 x oxaz C*H* + 2 x oxaz C*H*$_2$), 4.08 (mc, 1H; cod C*H*), 3.96 (mc, 1H; oxaz C*H*), 3.85 (mc,

1H; cod C*H*), 3.79 (mc, 2H; cod C*H*), 3.26 (mc, 2H; C*H*(CH_3)$_2$), 2.43-2.01 (m, 4H; cod CH_2), 2.33 (mc, 2H; cod CH_2), 2.00 (mc, 2H; cod CH_2), 1.18 (d, ^3J(H,H) = 7.1 Hz, 3H; CH(CH_3)$_2$), 1.14 (d, ^3J(H,H) = 7.1 Hz, 3H; CH(CH_3)$_2$), 0.94 (d, ^3J(H,H) = 6.8 Hz, 3H; CH(CH_3)$_2$), 0.87 (d, ^3J(H,H) = 6.9 Hz, 3H; CH(CH_3)$_2$).

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 154.4 (N*C*N), 151.0 (2C; pyr *C*H), 139.4 (1C; pyr *C*H), 127.6 (2C; pyr *C*H), 126.4 (N*C*O), 125.9 (N*C*O), 84.7 (cod *C*H), 83.6 (cod *C*H), 76.3 (oxaz *C*H_2), 76.2 (oxaz *C*H_2), 66.2 (cod *C*H), 62.8 (oxaz *C*H), 62.5 (cod *C*H), 61.9 (oxaz *C*H), 34.6 (cod *C*H_2), 33.2 (*C*H(CH_3)$_2$), 32.0 (*C*H(CH_3)$_2$), 31.8 (cod *C*H_2), 31.7 (cod *C*H_2), 29.2 (cod *C*H_2), 19.35 (CH(*C*H_3)$_2$), 19.27 (CH(*C*H_3)$_2$), 14.9 (CH(*C*H_3)$_2$), 14.7 (CH(*C*H_3)$_2$).

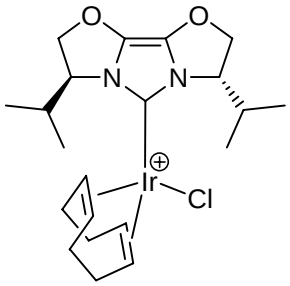
^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 295 K) : δ = -144.1 (sept, ^1J(P,F) = 711 Hz; PF_6);

IR (KBr): $\tilde{\nu}$ = 2963m, 2934m, 2890m, 2836w, 1757m, 1483m, 1466m, 1447m, 1428m, 1395m, 1377m, 1363m, 1337m, 1241w, 1198m, 1159w, 1118w, 1056w, 1000w, 978w, 929.0 m, 836s, 763m, 703m, 668w, 616w, 558m, 490w, 467w cm^{-1};

MS (FAB): *m/z* (%): 616 (100) [M – PF_6]$^+$, 535 (58);

EA calcd (%) for $C_{26}H_{37}F_6IrN_3O_2P$·(760.78): C 41.05, H 4.90, N 5.52; found: C 40.84, H 4.69, N 5.36.

(*S*,*S*)-[**(**η^4-1,5-cyclooctadiene**)**-(isopropyl-bioxazolin-ylidene)iridium(I)]-chloride **68**.



Schwesinger base BEMP (106 mg, 0.388 mmol) was added to a solution of [(η^4-cod)IrCl]$_2$ (130 mg, 0.194 mmol) and imidazolium salt **55** (150 mg, 0.388 mmol) in CH_2Cl_2 (10 ml). The reaction was stirred at room temperature for 2 hours then concentrated *in vacuo* to remove CH_2Cl_2. The crude product was purified by chromatography on silica gel eluting with 0.5% methanol in CH_2Cl_2 to yield a yellow solid (155 mg, 0.272 mmol, 70%).

$[\alpha]_D^{20}$ = +16 (c = 0.238, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 4.79 (mc, 3H; 2 x oxaz CH_2 + 1 x oxaz C*H*), 4.71-4.58 (m, 3H; 2 x oxaz CH_2 + 1 x cod C*H*), 4.48 (1 x cod C*H* + 1 x oxaz C*H*), 3.34-3.18

(m, 2H; C*H*(CH_3)$_2$), 3.14 (mc, 1H; cod C*H*), 3.02 (mc, 1H; cod C*H*), 2.23-2.04 (m, 4H; cod CH_2), 1.82-1.54 (m, 4H; cod CH_2), 1.04 (mc, 6H; CH(CH_3)$_2$), 0.90 (mc, 6H; CH(CH_3)$_2$);

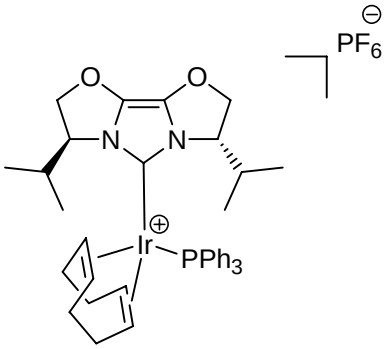
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 158.2 (N*C*N), 125.1 (N*C*O), 124.6 (N*C*O), 84.1 (cod *C*H), 83.8 (cod *C*H), 76.0 (cod *C*H_2), 75.7 (cod *C*H_2), 61.7 (oxaz *C*H), 60.8 (oxaz *C*H), 51.3 (cod *C*H), 50.2 (cod *C*H), 34.1 (cod *C*H_2), 33.5 (cod *C*H_2), 31.7 (*C*H(CH_3)$_2$), 29.9 (*C*H(CH_3)$_2$), 29.8 (cod *C*H_2), 29.3 (cod *C*H_2), 18.89 (CH(*C*H_3)$_2$), 18.86 (CH(*C*H_3)$_2$), 14.6 (CH(*C*H_3)$_2$), 14.5 (CH(*C*H_3)$_2$);

IR (KBr): $\tilde{\nu}$ = 2959m, 2932m, 2875m, 2828w, 1754m, 1464m, 1427s, 1378m, 1363m, 1337m, 1202m, 1117w, 1054w, 1002w, 959w, 931m, 883w, 859m, 830m, 740w, 704w, 620w, 520w, 476w, 432w, cm^{-1};

MS (FAB): *m/z* (%): 572 (50), 237 (100);

EA calcd (%) for $C_{21}H_{32}ClIrN_2O_2$·(572.16): C 44.08, H 5.64, N 4.90, O 5.59; found: C 44.02, H 5.50, N 4.82, O 5.41.

(*S*,*S*)-[**(**η^4-1,5-cyclooctadiene**)**-(isopropyl-bioxazolin-ylidene)-(triphenylphosphine)iridium(I)]-hexafluorophosphate **69**.



A solution of $AgPF_6$ (46 mg, 0.181 mmol) in THF (1 ml) was added to a solution of iridium complex **68** (130 mg, 0.181 mmol) in a mixture of CH_2Cl_2 and THF (2:1, 3 ml). The mixture was stirred at room temperature for 10 minutes then filtered to remove silver chloride. The filtrate was added to a solution of PPh_3 (48 mg, 0.181 mmol) in THF (1 ml). The reaction mixture was stirred at room temperature for 30 minutes and was concentrated *in vacuo* to give a red solid. The crude product was purified by chromatography on silica gel eluting with 1% MeOH in CH_2Cl_2 to yield a red solid (125 mg, 0.132 mmol, 73%).

$[\alpha]_D^{20}$ = -47 (c = 0.115, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.52 (mc, 3H; arom C*H*), 7.45 (mc, 6H; arom C*H*), 7.29 (mc, 6H; arom C*H*), 4.98 (mc, 1H; oxaz CH_2), 4.88 (mc, 1H; cod C*H*), 4.72 (mc,

1H; oxaz CH_2), 4.66 (mc, 1H; oxaz C*H*), 4.43-4.35 (m, 2H; 1 x oxaz CH_2 + 1 x cod C*H*), 3.88-3.78 (m, 2H; 1 x cod C*H* + 1 x oxaz CH_2), 3.47 (mc, 1H; cod C*H*), 2.97 (mc, 1H; oxaz C*H*), 2.81 (mc, 1H; C*H*(CH_3)$_2$), 2.50-2.31 (m, 3H; 2 x cod CH_2 + 1 x C*H*(CH_3)$_2$), 2.30-2.14 (m, 3H; cod CH_2), 2.07-1.92 (m, 2H; cod CH_2), 1.76 (mc, 1H; cod CH_2), 1.04 (d, ^3J(H,H) = 7.1 Hz, 3H; CH(CH_3)$_2$), 0.96 (d, ^3J(H,H) = 6.9 Hz, 3H; CH(CH_3)$_2$), 0.86 (d, ^3J(H,H) = 6.8 Hz, 3H; CH(CH_3)$_2$), 0.59 (d, ^3J(H,H) = 6.8 Hz, 3H; CH(CH_3)$_2$).

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 152.7 (d, ^2J(P,C) = 9.6 Hz; N*C*N), 133.9 (d, 6C, *J*(P,C) = 10.6 Hz; arom *C*H), 131.6 (d, 3C, *J*(P,C) = 1.9 Hz, arom *C*H), 130.6 (d, 3C, ^1J(P,C) = 50.4 Hz; arom *C*), 129.2 (d, 6C, *J*(P,C) = 10.1 Hz; arom *C*H), 126.6 (N*C*O), 126.2 (N*C*O), 87.3 (d, ^2J(P,C) = 12.5 Hz, cod *C*H), 86.9 (d, ^2J(P,C) = 11.5 Hz, cod *C*H), 81.8 (cod *C*H), 78.6 (cod *C*H), 76.4 (oxaz *C*H_2), 75.2 (oxaz *C*H_2), 62.8 (oxaz *C*H), 61.9 (oxaz *C*H), 32.6 (br, cod *C*H_2), 32.0 (br, cod *C*H_2), 31.9 (*C*H(CH_3)$_2$), 31.6 (*C*H(CH_3)$_2$), 30.2 (br, cod *C*H_2), 29.4 (br, cod *C*H_2), 20.1 (CH(*C*H_3)$_2$), 19.3 (CH(*C*H_3)$_2$), 15.5 (CH(*C*H_3)$_2$), 14.4 (CH(*C*H_3)$_2$).

^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 295 K) : δ = 19.4.9 (s), -144.9 (sept, ^1J(P,F) = 711 Hz; PF_6);

IR (KBr): $\tilde{\nu}$ = 3056w, 2962w, 2972w, 1752w, 1480w, 1435m, 1395w, 1376w, 1337w, 1200w, 1094w, 1056w, 998w, 974w, 920w, 840s, 750w, 697m, 558m, 532m, 512w, 455w, 421w cm^{-1};

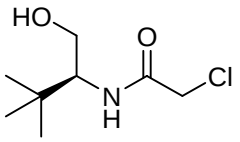
MS (ESI): *m/z* (%): 799.2 (100) [M – PF_6]$^+$;

EA calcd (%) for $C_{39}H_{47}F_6IrN_2O_2P_2$·(943.96): C 49.62, H 5.02; N 2.97, O 3.39; found C 50.09, H 5.36; N 3.00, O 3.68.

6.3 Oxazoline-imidazolin-2-ylidene ligands

6.3.1 Synthesis of chloroacetamides 78a-b

(*S*)-2-chloro-*N*-(1-hydroxymethyl-2,2-dimethyl-propyl)-acetamide **78a**



A solution of (*S*)-*tert*-leucinol (3.02 g, 25.8 mmol) and triethylamine (5.2 g, 51.6 mmol) in CH_2Cl_2 (100 ml) was cooled to -20°C under argon. Chloroacetyl chloride (2.91 g, 25.8 mmol) was added dropwise over 5 minutes. The cooling bath was removed and the reaction mixture was stirred at room temperature for 12 hours then concentrated *in vacuo*. Ethyl acetate was added (30 ml) and the mixture was filtered and concentrated *in* vacuo to remove the solvent. The crude product was purified by chromatography on silica gel eluting with AcOEt to yield a white solid (4.14 g, 21.4 mmol, 83%).

***R*$_f$ =** 0.57, AcOEt

m.p. 69-70°C;

$[\alpha]_D^{20}$ = -18.7 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 6.75 (br, 1H; NH), 4.10 (mc, 2H; ClC*H*$_2$), 3.86 (mc, 2H; C*H*$_2$OH + C*H*CC(CH$_3$)$_3$), 3.62 (mc, 1H; C*H*$_2$OH), 2.13 (br, 1H; O*H*), 0.97 (s, 9H; C(C*H*$_3$)$_3$);

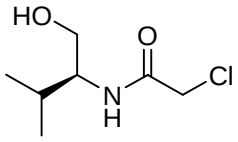
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 167.4 (NH*C*O), 63.1 (N*C*H$_2$OH), 60.5 (N*C*HC(CH$_3$)$_3$), 43.3 (Cl*C*H$_2$), 34.0 (*C*(CH$_3$)$_3$), 27.2 (C(*C*H$_3$)$_3$);

IR (KBr): $\tilde{\nu}$ = 3405mbr, 3277m, 2963m, 1665s, 1636s, 1531s, 1369w, 1276w, 1088w, 1049m, 911w, 771w, 666w cm^{-1};

MS (FAB): *m/z* (%): 194 (100) $[M + H]^+$;

EA calcd (%) for $C_8H_{16}ClNO_2$ (193.67): C 49.61, H 8.33, N 7.23, O 16.52; found: C 49.22, H 8.37, N 7.04, O 16.68.

(*S*)-2-chloro-*N*-(1-hydroxymethyl-2-methyl-propyl)-acetamide **78b**



Synthesis according to the previous general procedure using (*S*)-valinol (5.46 g, 53.0 mmol), triethylamine (5.52 g, 54.6 mmol) and chloroacetyl chloride (5.95 g, 52.7 mmol) yielded a colourless oil (8.42 g, 89%).

$\boldsymbol{R}_f$ = 0.45, AcOEt;

$[\alpha]_D^{20}$ = -34.1 (c = 1.00, CH_2Cl_2);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 6.75 (br, 1H; N*H*), 4.09 (mc, 2H; ClCH_2), 3.76 (mc, 1H; NC*H*CH$(CH_3)_2$), 3.71 (mc, 2H; CH_2OH), 2.41 (br, 1H; O*H*), 1.94 (mc, 1H; C*H*$(CH_3)_2$), 0.98 (d, ^3J(H,H) = 6.9 Hz, 3H; CH(CH_3)$_2$), 0.90 (d, ^3J(H,H) = 7.1 Hz, 3H; CH(CH_3)$_2$);

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 166.7 (*C*ONH), 63.4, (*C*H_2OH), 57.4 (N*C*HCH$(CH_3)_2$), 42.8 (Cl*C*H_2), 28.9 (*C*H$(CH_3)_2$), 19.5 (CH(*C*H_3)$_2$), 18.6 (CH(*C*H_3)$_2$);

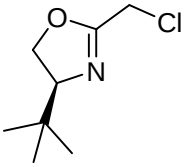
IR (NaCl): $\tilde{\nu}$ = 3297mbr, 2963m, 1660sbr, 1542mbr, 1466w, 1243w, 1082w, 776w cm^{-1};

MS (FAB): *m/z* (%): 180 (100) $[M + H]^+$;

EA calcd (%) for $C_7H_{14}ClNO_2$ (179.64): C 46.80, H 7.86, N 7.80; found: C 46.93, H 7.64, N 7.71.

6.3.2 Synthesis of chloromethyloxazolines 79a-b

(*S*)-4-*tert*-butyl-2-chloromethyl-4,5-dihydro-oxazole **79a**



A solution of chloroacetamide **78a** (1.29 g, 6.65 mmol) and methyl-*N*-triethylammoniosulfonyl-carbamate (1.74 g, 7.32 mmol) in THF (20 ml) was refluxed for 12 hours. The reaction mixture was concentrated *in vacuo*. The residue was diluted with dichloromethane and extracted three times with water. The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The crude product was purified by distillation (50°C, 0.1 mbar) to yield a colourless oil (1.45 g, 8.25 mmol, 50%).

b.p. 50°C at 0.1 mbar;

$[\alpha]_D^{20}$ = -108.5 (c = 0.94, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 4.28 (mc, 1H; CH_2O), 4.15 (mc, 1H; CH_2O), 4.10 (mc, 2H; ClCH_2), 3.91 (mc, 1H; NCHC(CH_3)$_3$), 0.89 (s, 9H; C(CH_3)$_3$);

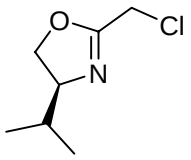
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 162.4 (O*C*N), 76.1 (N*C*HCH(CH_3)$_2$), 69.8 (*C*H_2O), 36.5 (Cl*C*H_2), 33.8 (*C*(CH_3)$_3$), 25.8 (C(*C*H_3)$_3$);

IR (NaCl): $\tilde{\nu}$ = 2957s, 2906m, 2870m, 1671s, 1479m, 1430w, 1395w, 1360m, 1243m, 1155w, 983s, 944w, 892w, 733w cm^{-1};

MS (FAB, Xe 8 kV): *m/z* (%): 176 (100) $[M + H]^+$;

EA calcd (%) for $C_8H_{14}ClNO$ (175.66): C 54.70, H 8.03, N 7.97; found: C 53.83, H 7.90, N 8.03

(*S*)-2-chloromethyl-4-isopropyl-4,5-dihydro-oxazole **79b**



Synthesis according to the previous general procedure using chloroacetamide **78b** (4.10 g, 22.8 mmol) and Burgess reagent (5.61 g, 23.5 mmol) yielded a colourless oil (2.42 g, 66%, 15.0 mmol).

b.p. 42°C at 0.05 mbar;

$[\alpha]_D^{20}$ = -98.9 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 4.33 (mc, 1H; CH_2O), 4.09 (mc, 2H; ClCH_2), 4.04 (mc, 1H; CH_2O), 3.95 (mc, 1H; NCHCH(CH_3)$_2$), 1.76 (mc, 1H; CH(CH_3)$_2$), 0.95 (d, ^3J(H,H) = 7.0 Hz, 3H; CH(CH_3)$_2$), 0.87 (d, ^3J(H,H) = 7.0 Hz, 3H; CH(CH_3)$_2$);

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 162.3 (O*C*N), 72.4 (N*C*HCH(CH_3)$_2$), 71.2 (*C*H_2O), 36.4 (Cl*C*H_2), 32.5 (*C*H(CH_3)$_2$), 18.7 (CH(*C*H_3)$_2$), 18.1 (CH(*C*H_3)$_2$);

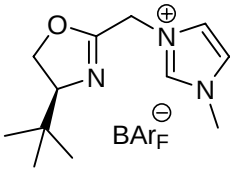
IR (NaCl): $\tilde{\nu}$ = 2961s, 1669s, 1468w, 1360m, 1243m, 1155w, 982s, 891w, 718w cm^{-1};

MS (FAB, Xe 8 kV): *m/z* (%): 162 (100) $[M + H]^+$;

EA calcd (%) for $C_7H_{12}ClNO$ (161.63): C 52.02, H 7.48, N 8.67; found: C 51.57, H 7.49, N 8.50.

6.3.3 Synthesis of imidazolium salts 80a-g

(*S*)-[1-(4-*tert*-butyl-4,5-dihydro-oxazol-2-ylmethyl)-3-methyl-3*H*-imidazol-1-ium]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **80a**



A solution of chloromethyloxazoline **79a** (235 mg, 1.33 mmol) and 1-methyl-1*H*-imidazole (93 mg, 1.33 mmol) in DMF (0.4 ml) was heated at 80°C for 8 hours. The reaction mixture was concentrated *in vacuo* at 80°C and the residue was diluted in CH_2Cl_2 (5 ml). $NaBAr_F$ (1.18 g, 1.33 mmol) was added to the solution which was stirred at room temperature for 30 minutes. The mixture was filtered and concentrated *in vacuo*. The crude product was purified by chromatography on a plug of silica gel eluting with CH_2Cl_2 (1L) to yield a white solid (1.13 g, 1.03 mmol, 78%).

m.p. 103-104°C;

$[\alpha]_D^{20}$ = -8.2 (c = 0.50, $CHCl_3$);

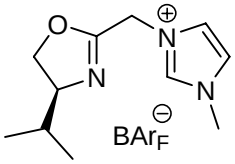
^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 8.31 (s, 1H; NC*H*N), 7.69 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.15 (mc, 1H; imid C*H*), 6.95 (mc, 1H; imid C*H*), 4.71 (mc, 2H; NCH_2), 4.27 (mc, 1H; oxaz CH_2), 4.14 (mc, 1H; oxaz CH_2), 3.88 (mc, 1H; oxaz C*H*), 3.70 (s, 3H, NCH_3), 0.82 (s, 9H; *t*Bu CH_3);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 162.1 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 158.1 (O*C*N), 135.7 (N*C*HN), 135.1 (br, 8C; BAr_F *ortho C*H), 129.3 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.9 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 124.2 (imid *C*H), 123.8 (imid *C*H), 117.9 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 76.4 (oxaz *C*H), 71.0 (oxaz *C*H_2), 46.7 (N*C*H_2), 37.0 (N*C*H_3), 33.8 (*t*Bu *C*), 25.8 (3C; *t*Bu *C*H_3);

IR (KBr): $\tilde{\nu}$ = 3185w, 2967w, 1686w, 1610w, 1356m, 1277s, 1115bs, 887w, 838w, 743w, 711w, 682w, 671w, 623w cm^{-1}; MS (FAB): *m/z* (%): 222 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{44}H_{32}BF_{24}N_3O$ (1085.52): C 48.68, H 2.97, N 3.87; found: C 48.72, H 2.99, N 3.84.

(*S*)-[1-(4-isopropyl-4,5-dihydro-oxazol-2-ylmethyl)-3-methyl-3*H*-imidazol-1-ium]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **80b**



Synthesis according to the previous general procedure using chloromethyloxazoline **79b** (623 mg, 3.85 mmol), methylimidazole (316 mg, 3.85 mmol) and $NaBAr_F$ (3.41 g, 3.85 mmol) yielded a white solid (3.02 g, 73%, 2.81 mmol).

m.p. 93-94°C;

$[\alpha]_D^{20}$ = -8.7 (c = 0.50, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 8.31 (s, 1H; NC*H*N), 7.69 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.13 (mc, 1H; imid C*H*), 6.94 (mc, 1H; imid C*H*), 4.69 (mc, 2H; NCH_2), 4.33 (mc, 1H; oxaz CH_2), 4.03 (mc, 1H; oxaz CH_2), 3.89 (mc, 1H; oxaz C*H*), 3.70 (s, 3H, NCH_3), 1.67 (mc, 1H; *i*Pr CH_3), 0.89 (d, ^3J(H,H) = 6.6 Hz, 3H; *i*Pr CH_3), 0.82 (d, ^3J(H,H) = 6.7 Hz, 3H; *i*Pr CH_3);

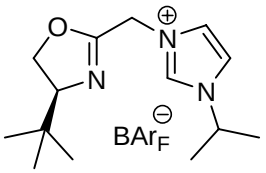
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 157.9 (O*C*N), 135.7 (N*C*HN), 134.7 (br, 8C; BAr_F *ortho C*H), 129.1 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.7 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.8 (imid *C*H), 123.3 (imid *C*H), 117.6 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 72.9 (oxaz *C*H), 72.5 (oxaz *C*H_2), 46.2 (N*C*H_2), 36.6 (N*C*H_3) 32.4 (*i*Pr *C*H), 18.5 (*i*Pr *C*H_3), 18.1 (*i*Pr *C*H_3);

IR (KBr): $\tilde{\nu}$ = 3182w, 2969w, 1689w, 1610w, 1358m, 1280s, 1120bs, 889w, 835w, 740w, 712w, 674w, 621w cm^{-1};

MS (FAB): *m/z* (%): 208 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{43}H_{30}BF_{24}N_3O$ (1071.49): C 48.20, H 2.82, N 3.92; found: C 48.16, H 2.90, N 3.70.

(*S*)-[1-(4-*tert*-butyl-4,5-dihydro-oxazol-2-ylmethyl)-3-isopropyl-3*H*-imidazol-1-ium]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **80c**



Synthesis according to the previous general procedure using chloromethyloxazoline **79a** (150 mg, 0.854 mmol), isopropylimidazole (94 mg, 0.854 mmol) and $NaBAr_F$ (757 mg, 0.854 mmol) yielded a white solid (608 mg, 64%, 0.546 mmol)

m.p. 102-103°C;

$[\alpha]_D^{20}$ = -7.1 (c = 0.50, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.46 (s, 1H; NC*H*N), 7.68 (mc, 8H; BAr_F *ortho* C*H*), 7.52 (mc, 4H; BAr_F para C*H*), 7.15 (mc, 1H; imid C*H*), 7.11 (mc, 1H; imid C*H*), 4.71 (mc, 2H; NCH_2), 4.41 (mc, 1H; *i*Pr C*H*), 4.26 (mc, 1H; oxaz CH_2), 4.12 (mc, 1H; oxaz CH_2), 3.88 (mc, 1H; oxaz C*H*), 1.47 (mc, 6H; *i*Pr CH_3), 0.81 (s, 9H; CH_3 *t*Bu);

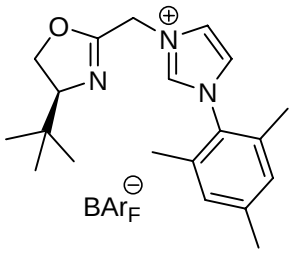
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 161.6 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 158.0 (O*C*N), 134.7 (br, 8C; BAr_F *ortho C*H), 133.3 (N*C*HN), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.6 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.4 (imid *C*H), 120.4 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 75.9 (oxaz *C*H), 70.6 (oxaz *C*H_2), 54.6 (*i*Pr *C*H), 46.2 (N*C*H_2), 33.4 (*t*Bu *C*), 25.4 (3C; *t*Bu *C*H_3), 22.4 (2C; *i*Pr *C*H_3);

IR (KBr): $\tilde{\nu}$ = 3184w, 2982w, 1692w, 1610w, 1591w, 1561w, 1467w, 1356m, 1277s, 1124bs, 976w, 935w, 886w, 712w, 682w cm^{-1};

MS (FAB): *m/z* (%): 250 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{46}H_{36}BF_{24}N_3O$ (1113.57): C 49.62, H 3.26, N 3.77; found: C 49.51, H 3.30, N 3.74.

(*S*)-[1-(4-*tert*-butyl-4,5-dihydro-oxazol-2-ylmethyl)-3-(2,4,6-trimethyl-phenyl)-3*H*-imidazol-1-ium]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **80d**



Synthesis according to the previous general procedure using chloromethyloxazoline **79a** (253 mg, 1.44 mmol), mesitylimidazole (268 mg, 1.44 mmol) and $NaBAr_F$ (1.28 g, 1.44 mmol) yielded a white solid (1.00 g, 58%, 0.840 mmol).

m.p. 119-120°C;

$[\alpha]_D^{20}$ = -3.4 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.45 (s, 1H; NC*H*N), 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.52 (mc, 4H; BAr_F para C*H*), 7.32 (mc, 1H; imid C*H*), 7.18 (mc, 1H; imid C*H*), 4.85 (mc, 2H; NCH_2), 4.30 (mc, 1H; oxaz CH_2), 4.16 (mc, 1H; oxaz CH_2), 3.87 (mc, 1H; oxaz C*H*), 2.33 (mc, 3H; $C_{arom}CH_3$), 1.95 (mc, 6H; $C_{arom}CH_3$), 0.79 (s, 9H; *t*Bu CH_3);

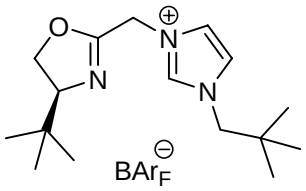
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 161.8 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 158.7 (O*C*N), 142.9 (arom *C*), 136.6 (N*C*HN), 134.9 (br, 8C; BAr_F *ortho C*H), 133.8 (2C; arom *C*), 130.4 (2C; arom *C*H), 129.8 (arom *C*), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.6 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 124.1 (imid *C*H), 124.0 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 75.9 (oxaz *C*H), 71.1 (oxaz *C*H_2), 46.6 (N*C*H_2), 33.5 (*t*Bu *C*), 25.5 (3C; *t*Bu *C*H_3), 21.1 ($C_{arom}CH_3$), 16.9 (2C; $C_{arom}CH_3$);

IR (KBr): $\tilde{\nu}$ = 3162w, 2968w, 1686w, 1611w, 1557w, 1561w, 1481w, 1356m, 1277s, 1121bs, 971w, 930w, 888w, 837w, 745w, 712w, 670w cm^{-1};

MS (FAB): *m/z* (%): 326 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{52}H_{40}BF_{24}N_3O$ (1189.67): C 52.50, H 3.39, N 3.53; found: C 52.53, H 3.33, N 3.53.

(*S*)-[1-(4-*tert*-butyl-4,5-dihydro-oxazol-2-ylmethyl)-3-(2,2-dimethyl-propyl)-3*H*-imidazol-1-ium]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **80e**



Synthesis according to the previous general procedure using chloromethyloxazoline **79a** (154 mg, 0.876 mmol), neopentylimidazole (121 mg, 0.876 mmol) and $NaBAr_F$ (776 mg, 0.876 mmol) yielded a white solid (640 mg, 64%, 0.561 mmol).

m.p. 114-115°C;

$[\alpha]_D^{20}$ = -6.0 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.37 (s, 1H; NC*H*N), 7.69 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.09 (mc, 1H; imid C*H*), 6.99 (mc, 1H; imid C*H*), 4.71 (mc, 2H; CH_2), 4.28 (mc, 1H; oxaz CH_2), 4.13 (mc, 1H; oxaz CH_2), 3.83 (mc, 1H; oxaz C*H*), 3.79 (mc, 2H, NCH_2C$(CH_3)_3$), 0.92 (s, 9H, $NCH_2C(CH_3)_3$), 0.79 (s, 9H; *t*Bu CH_3);

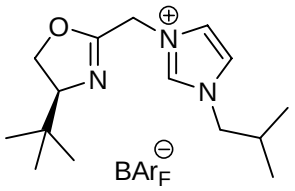
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 158.3 (O*C*N), 135.7 (N*C*HN), 134.7 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.6 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.5 (imid *C*H), 123.0 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 75.8 (oxaz *C*H), 70.8 (oxaz *C*H_2), 62.6 (N*C*$H_2C(CH_3)_3$), 46.2 (N*C*H_2), 33.3 (*t*Bu *C*), 32.5 (NCH_2*C*$(CH_3)_3$), 26.5 (3C; NCH_2C(*C*$H_3)_3$), 25.4 (3C; *t*Bu *C*H_3);

IR (KBr): $\tilde{\nu}$ = 3186w, 2970w, 1687w, 1610w, 1480w, 1357m, 1279s, 1125bs, 898w, 837w, 741w, 714w, 675w, cm^{-1};

MS (FAB): *m/z* (%): 278 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{48}H_{40}BF_{24}N_3O$ (1141.62): C 50.50, H 3.53, N 3.68; found: C 50.60, H 3.52, N 3.63.

(*S*)-[1-(4-*tert*-butyl-4,5-dihydro-oxazol-2-ylmethyl)-3-isobutyl-3*H*-imidazol-1-ium]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **80f**



Synthesis according to the previous general procedure using chloromethyloxazoline **79a** (154 mg, 0.876 mmol), isobutylimidazole (108 mg, 0.876 mmol) and $NaBAr_F$ (776 mg, 0.876 mmol) yielded a white solid (621 mg, 63%, 0.551 mmol).

m.p. 96-97°C;

$[\alpha]_D^{20}$ = -6.5 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.34 (s, 1H; NC*H*N), 7.69 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.11 (mc, 1H; imid C*H*), 6.99 (mc, 1H; imid C*H*), 4.70 (mc, 2H; NCH_2), 4.28 (mc, 1H; oxaz CH_2), 4.14 (mc, 1H; oxaz CH_2), 3.87 (mc, 1H; oxaz C*H*), 3.81 (mc, 2H, NCH_2CH(CH_3)$_2$), 2.01 (mc, 1H, $NCH_2CH(CH_3)_2$), 0.89 (mc, 6H, $NCH_2CH(CH_3)_2$), 0.80 (s, 9H; *t*Bu CH_3);

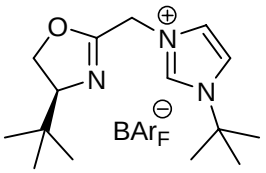
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 158.2 (O*C*N), 135.0 (N*C*HN), 134.7 (br, 8C; BAr_F *ortho C*H), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.6 (imid *C*H), 122.4 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 75.8 (oxaz *C*H), 70.7 (oxaz *C*H_2), 58.0 (N*C*H_2CH(CH_3)$_2$), 46.2 (N*C*H_2), 33.4 (*t*Bu *C*), 29.4 ($NCH_2CH(CH_3)_2$), 25.5 (3C; *t*Bu *C*H_3), 18.9 (2C; $NCH_2CH(CH_3)_2$);

IR (KBr): $\tilde{\nu}$ = 3179w, 2971w, 1687w, 1610w, 1473w, 1357m, 1279s, 1123bs, 953w, 897w, 837w, 715w, 675w, cm^{-1};

MS (FAB): *m/z* (%): 264 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{47}H_{38}BF_{24}N_3O$ (1127.60): C 50.06, H 3.40, N 3.73; found: C 50.05, H 3.26, N 3.71.

(*S*)-[3-*tert*-butyl-1-(4-tert-butyl-4,5-dihydro-oxazol-2-ylmethyl)-3*H*-imidazol-1-ium]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **80g**



Synthesis according to the previous general procedure using chloromethyloxazoline **79a** (150 mg, 0.854 mmol), *tert*-butylimidazole (106 mg, 0.854 mmol) and $NaBAr_F$ (756 g, 0.854 mmol) yielded a white solid (652 mg, 68%, 0.578 mmol).

m.p. 95-96°C;

$[\alpha]_D^{20}$ = -6.9 (c = 0.50, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 8.55 (s, 1H; NC*H*N), 7.69 (mc, 8H; BAr_F *ortho* C*H*), 7.52 (mc, 4H; BAr_F para C*H*), 7.21 (mc, 1H; imid C*H*), 7.16 (mc, 1H; imid C*H*), 4.72 (mc, 2H; NCH_2), 4.27 (mc, 1H; oxaz CH_2), 4.13 (mc, 1H; oxaz CH_2), 3.89 (mc, 1H; oxaz C*H*), 2.01 (mc, 1H, $NCH_2CH(CH_3)_2$), 1.55 (s, 9H; *t*Bu_{imid} CH_3), 0.81 (s, 9H; *t*Bu_{oxaz} CH_3);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 158.5 (O*C*N), 134.7 (br, 8C; BAr_F *ortho C*H), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 133.4 (N*C*HN), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.6 (imid *C*H), 120.2 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 76.3 (oxaz *C*H), 71.0 (oxaz *C*H_2), 62.0 (*t*Bu_{imid} *C*), 46.6 (N*C*H_2), 33.8 (*t*Bu_{oxaz} *C*), 29.8 (3C; *t*Bu_{imid} *C*H_3), 25.8 (3C; *t*Bu_{oxaz} *C*H_3);

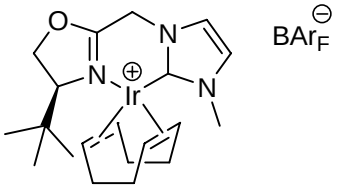
IR (KBr): $\tilde{\nu}$ = 3186w, 2978w, 1695w, 1610w, 1468w, 1356m, 1277s, 1124bs, 935w, 888w, 838w, 712w, 682w, 671w cm^{-1};

MS (FAB): *m/z* (%): 264 (100) $[M - BAr_F]^+$;

EA calcd (%) for $C_{47}H_{38}BF_{24}N_3O$ (1127.60): C 50.06, H 3.40, N 3.73; found: C 49.69, H 3.26, N 3.45.

6.3.4 Synthesis of iridium complexes 6a-f

(*S*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(4-*tert*-butyl-4,5-dihydro-oxazol-2-ylmethyl)-3-methyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **81a**



Freshly sublimed NaO*t*Bu (14.3 mg, 0.148 mmol) was added to a solution of imidazolium salt **80a** (161 mg, 0.148 mmol) and [(η^4-cod)IrCl]$_2$ (50 mg, 0.074 mmol) in THF (10 ml). The reaction mixture was stirred at room temperature for 3 hours then concentrated *in vacuo* to remove the solvent. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2 to yield a yellow/orange solid (134 mg, 0.096 mmol, 65%).

$[\alpha]_D^{20}$ = +48 (c = 0.159, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.81 (mc, 1H; imid C*H*), 6.79 (mc, 1H; imid C*H*), 4.98 (mc, 1H; NCH_2), 4.61 (mc, 1H; oxaz CH_2), 4.49 (mc, 1H; cod C*H*), 4.38 (mc, 2H; NCH_2 + oxaz CH_2), 4.15 (mc, 2H; cod C*H*), 3.86 (mc, 1H; cod C*H*), 3.80 (mc, 1H; oxaz C*H*), 3.74 (s, 3H, NCH_3), 2.29 (mc, 2H; cod CH_2), 2.11 (mc, 2H; cod CH_2), 2.00 (mc, 2H; cod CH_2), 1.75 (mc, 1H; cod CH_2), 1.63 (mc, 1H; cod CH_2), 0.73 (s, 9H; *t*Bu CH_3);

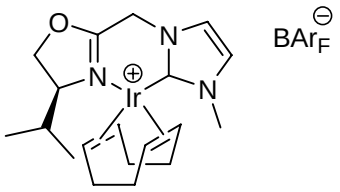
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 174.1 (N*C*N), 165.1 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.8 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.5 (imid *C*H), 121.1 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 85.4 (cod *C*H), 81.9 (cod *C*H), 73.3 (oxaz *C*H), 72.8 (oxaz *C*H_2), 64.4 (cod *C*H), 59.0 (cod *C*H), 46.8 (N*C*H_2), 38.0 (N*C*H_3), 34.0 (cod *C*H_2), 33.5 (*t*Bu *C*), 31.1 (cod *C*H_2), 29.9 (cod *C*H_2), 28.3 (cod *C*H_2), 25.1 (3C; *t*Bu *C*H_3);

IR (KBr): $\tilde{\nu}$ = 2971w, 1648w, 1610w, 1435w, 1355m, 1277s, 1124bs, 960w, 894w, 839w, 712w, 682w, 671w cm^{-1};

MS (FAB): *m/z* (%): 522 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{52}H_{43}BF_{24}IrN_3O$ (1384.91): C 45.10, H 3.13, N 3.03; found: C 45.25, H 3.24, N 2.87.

(*S*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(4-isopropyl-4,5-dihydro-oxazol-2-ylmethyl)-3-methyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **81b**



Synthesis according to the previous general procedure using imidazolium salt **80b** (200 mg, 0.187 mmol), [(η^4-cod)IrCl]$_2$ (63 mg, 0.094 mmol) and NaO*t*Bu (18 mg, 0.187 mmol) yielded an orange solid (129 mg, 50%, 0.094 mmol).

$[\alpha]_D^{20}$ = +33 (c = 0.165, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.76 (mc, 2H; imid C*H*), 4.91 (mc, 1H; NCH_2), 4.55-4.30 (m, 4H; 1 x cod C*H* + 2 x oxaz CH_2 + 1 x NCH_2), 4.15 (mc, 2H; cod C*H*), 4.00 (mc, 1H; oxaz C*H*), 3.94 (mc, 1H; cod C*H*), 3.75 (s, 3H, NCH_3), 2.37 (mc, 1H; cod CH_2), 2.26 (mc, 1H; cod CH_2), 2.16 (mc, 2H; cod CH_2), 2.00 (mc, 2H; cod CH_2), 1.80 (mc, 1H; *i*Pr C*H*), 1.71 (mc, 1H; cod CH_2), 1.60 (mc, 1H; cod CH_2), 0.77 (d, ^3J(H,H) = 6.9 Hz, 3H; *i*Pr CH_3), 0.64 (d, ^3J(H,H) = 7.0 Hz, 3H; *i*Pr CH_3);

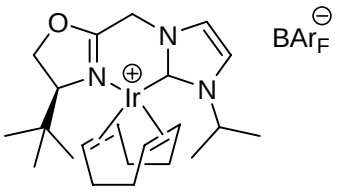
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 174.3 (N*C*N), 165.4 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 135.8 (br, 8C; BAr_F *ortho C*H), 129.1 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 124.1 (imid *C*H), 121.5 (imid *C*H), 117.8 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 84.6 (cod *C*H), 82.9 (cod *C*H), 72.4 (oxaz *C*H_2), 69.6 (oxaz *C*H), 65.7 (cod *C*H), 60.1 (cod *C*H), 47.0 (N*C*H_2), 38.6 (N*C*H_3), 34.7 (cod *C*H_2), 32.1 (*i*Pr *C*H), 31.2 (cod *C*H_2), 31.0 (cod *C*H_2), 28.4 (cod *C*H_2), 17.9 (3C; *i*Pr *C*H_3), 16.3 (3C; *i*Pr *C*H_3);

IR (KBr): $\tilde{\nu}$ = 2969w, 2890w, 1652w, 1610w, 1456w, 1430w, 1355m, 1277s, 1124bs, 962w, 893w, 839w, 713w, 681w, 671w cm^{-1};

MS (FAB): *m/z* (%): 508 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{51}H_{41}BF_{24}IrN_3O$ (1370.88): C 44.68, H 3.01, N 3.07; found: C 44.57, H 3.19, N 3.13.

(*S*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(4-*tert*-butyl-4,5-dihydro-oxazol-2-ylmethyl)-3-isopropyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **81c**



Synthesis according to the previous general procedure using imidazolium salt **80c** (166 mg, 0.148 mmol), [(η^4-cod)IrCl]$_2$ (50 mg, 0.074 mmol) and NaO*t*Bu (14 mg, 0.148 mmol) yielded of an orange solid (96 mg, 46%, 0.068 mmol).

$[\alpha]_D^{20}$ = +36 (c = 0.128, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.71 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.95 (mc, 1H; imid C*H*), 6.85 (mc, 1H; imid C*H*), 5.02 (mc, 1H; NCH_2), 4.86 (mc, 1H; C*H* *i*Pr), 4.56 (mc, 2H; oxaz CH_2 + cod C*H*), 4.38 (mc, 2H; NCH_2 + oxaz CH_2), 4.11 (mc, 1H; cod C*H*), 3.92 (mc, 1H; cod C*H*), 3.79 (mc, 2H; oxaz C*H* + cod C*H*), 2.36 (mc, 1H; cod CH_2), 2.24 (mc, 2H; cod CH_2), 2.16 (mc, 1H; cod CH_2), 2.09 (mc, 1H; cod CH_2), 1.96 (mc, 1H; cod CH_2), 1.65 (mc, 1H; cod CH_2), 1.55 (mc, 1H; cod CH_2), 1.39 (d, ^3J(H,H) = 7.0 Hz, 3H; *i*Pr CH_3), 1.35 (d, ^3J(H,H) = 7.0 Hz, 3H; *i*Pr CH_3), 0.71 (s, 9H; *t*Bu CH_3);

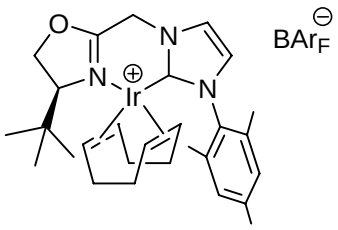
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 173.9 (N*C*N), 165.2 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.8 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 122.1 (imid *C*H), 117.8 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 85.3 (cod *C*H), 82.1 (cod *C*H), 73.4 (oxaz *C*H), 72.9 (oxaz *C*H_2), 65.8 (cod *C*H), 58.0 (cod *C*H), 52.5 (*i*Pr *C*H), 46.8 (N*C*H_2), 34.8 (cod *C*H_2), 33.5 (*t*Bu *C*), 30.7 (cod *C*H_2), 30.5 (cod *C*H_2), 27.6 (cod *C*H_2), 25.0 (3C; *t*Bu *C*H_3), 23.7 (*i*Pr *C*H_3), 23.6 (*i*Pr *C*H_3);

IR (KBr): $\tilde{\nu}$ = 2971w, 1651w, 1610w, 1440w, 1354m, 1272s, 1124bm, 960w, 897w, 839w, 712w, 682w, 670w cm^{-1};

MS (FAB): *m/z* (%): 550 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{54}H_{47}BF_{24}IrN_3O$ (1412.96): C 45.90, H 3.35, N 2.97; found: C 46.02, H 3.28, N 2.75.

(*S*)-{(η^4-1,5-cyclooctadiene)-[1-(4-*tert*-butyl-4,5-dihydro-oxazol-2-ylmethyl)-3-(2,4,6-trimethyl-phenyl)-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **81d**



Synthesis according to the previous general procedure using imidazolium salt **80d** (176 mg, 0.148 mmol), [(η^4-cod)IrCl]$_2$ (50 mg, 0.074 mmol) and NaO*t*Bu (14 mg, 0.148 mmol) yielded an orange solid (100 mg, 45%, 0.067 mmol).

$[\alpha]_D^{20}$ = +45 (c = 0.116, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.71 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.03 (mc, 1H, arom C*H*), 7.00 (mc, 1H; imid C*H*), 6.96 (mc, 1H, arom C*H*), 6.85 (mc, 1H; imid C*H*), 5.04 (mc, 1H; NCH_2), 4.65 (mc, 1H; oxaz CH_2), 4.48 (mc, 1H; NCH_2), 4.38 (mc, 1H; oxaz CH_2), 4.22 (mc, 2H; cod C*H*), 3.85 (mc, 1H; oxaz C*H*), 3.57 (mc, 1H; cod C*H*), 2.92 (mc, 1H; cod C*H*), 2.34 (s, 3H, $C_{arom}CH_3$), 2.06 (mc, 4H; 1 x cod CH_2 + $C_{arom}CH_3$), 1.97 (mc, 5H; 2 x cod CH_2+ $C_{arom}CH_3$), 1.55 (mc, 5H; cod CH_2), 0.87 (s, 9H; *t*Bu CH_3);

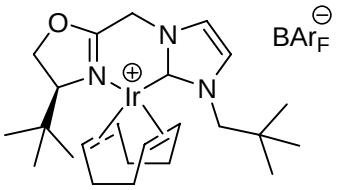
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 172.6 (N*C*N), 165.3 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 140.5 (arom *C*), 134.8 (br, 8C; BAr_F *ortho* *C*H), 134.6 (arom *C*), 134.5 (arom *C*), 134.4 (arom *C*), 129.6 (arom *C*H), 129.4 (arom *C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (imid *C*H), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 121.0 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 85.6 (cod *C*H), 79.5 (cod *C*H), 72.6 (oxaz *C*H_2), 72.4 (oxaz *C*H), 63.4 (cod *C*H), 62.3 (cod *C*H), 46.7 (N*C*H_2), 33.8 (*t*Bu *C*), 33.5 (cod *C*H_2), 31.8 (cod *C*H_2), 30.3 (cod *C*H_2), 27.6 (cod *C*H_2), 25.2 (3C; *t*Bu *C*H_3), 21.0 (C_{arom} *C*H_3), 18.6 (C_{arom} *C*H_3), 17.6 (C_{arom} *C*H_3);

IR (KBr): $\tilde{\nu}$ = 2967w, 1648w, 1611w, 1483w, 1443w, 1414w, 1355m, 1279s, 1124bm, 962w, 886w, 839w, 744w, 714w, 682w, 670w cm^{-1};

MS (FAB): *m/z* (%): 626 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{60}H_{51}BF_{24}IrN_3O$ (1489.06): C 48.40, H 3.45, N 2.82; found: C 48.37, H 3.47, N 2.59.

(*S*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(4-*tert*-butyl-4,5-dihydro-oxazol-2-ylmethyl)-3-(2,2-dimethyl-propyl)-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **81e**



Synthesis according to the previous general procedure using imidazolium salt **80e** (170 mg, 0.148 mmol), [(η^4-cod)IrCl]$_2$ (50 mg, 0.074 mmol) and NaO*t*Bu (14 mg, 0.148 mmol) yielded an orange solid (100 mg, 47%, 0.070 mmol).

$[\alpha]_D^{20}$ = +31 (c = 0.133, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.91 (mc, 1H; imid C*H*), 6.81 (mc, 1H; imid C*H*), 4.99 (mc, 1H; NCH_2), 4.59 (mc, 1H; oxaz CH_2), 4.38 (mc, 3H; cod C*H* + CH_2 + oxaz CH_2), 4.17 (mc, 1H; cod C*H*), 4.12 (mc, 1H; cod C*H*), 3.89 (mc, 3H; oxaz C*H* + cod C*H* + NCH_2C$(CH_3)_3$), 3.65 (mc, 3H, NCH_2C$(CH_3)_3$), 2.35 (mc, 1H; cod CH_2), 2.20 (mc, 2H; cod CH_2), 2.10 (mc, 1H; cod CH_2), 2.00 (mc, 2H; cod CH_2), 1.61 (mc, 1H; cod CH_2), 1.50 (mc, 1H; cod CH_2), 0.92 (s, 9H, NCH$_2$C$(CH_3)_3$), 0.80 (s, 9H; *t*Bu CH_3);

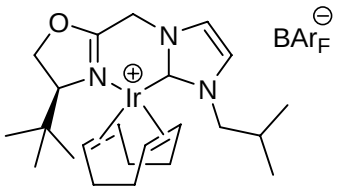
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 173.8 (N*C*N), 164.7 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.8 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F$_3$), 123.7 (imid *C*H), 120.8 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 84.0 (cod *C*H), 79.2 (cod *C*H), 73.2 (oxaz *C*H), 72.6 (oxaz *C*H$_2$), 64.2 (cod *C*H), 61.1 (N*C*H$_2$C$(CH_3)_3$), 60.1 (cod *C*H), 46.8 (N*C*H$_2$), 34.2 (cod *C*H$_2$), 33.6 (*t*Bu *C*), 32.6 (NCH$_2$*C*$(CH_3)_3$), 30.7 (cod *C*H$_2$), 30.2 (cod *C*H$_2$), 28.1 (3C; NCH$_2$C(*C*H$_3)_3$), 28.0 (cod *C*H$_2$), 25.2 (3C; *t*Bu *C*H$_3$);

IR (KBr): $\tilde{\nu}$ = 2967w, 1651w, 1611w, 1478w, 1441w, 1357m, 1279s, 1128bs, 890w, 838w, 714w, 674w cm^{-1};

MS (FAB): *m/z* (%): 578 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{56}H_{51}BF_{24}IrN_3O$ (1441.01): C 46.68, H 3.57, N 2.92; found: C 46.79, H 3.68, N 2.99.

(*S*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(4-*tert*-butyl-4,5-dihydro-oxazol-2-ylmethyl)-3-isobutyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **81f**



Synthesis according to the previous general procedure using imidazolium salt **80f** (168 mg, 0.148 mmol), [(η^4-cod)IrCl]$_2$ (50 mg, 0.074 mmol) and NaO*t*Bu (14 mg, 0.148 mmol) yielded an orange solid (93 mg, 44%, 0.065 mmol).

$[\alpha]_D^{20}$ = +36 (c = 0.138, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.83 (mc, 1H; imid C*H*), 6.80 (mc, 1H; imid C*H*), 4.99 (mc, 1H; NCH_2), 4.61 (mc, 1H; oxaz CH_2), 4.45 (mc, 1H; cod C*H*), 4.38 (mc, 2H; NCH_2 + oxaz CH_2), 4.13 (mc, 1H; cod C*H*), 4.05 (mc, 1H; cod C*H*), 3.91 (mc, 2H; cod C*H* + NCH_2CH$(CH_3)_2$), 3.81 (mc, 1H; oxaz C*H*),), 3.57 (mc, 3H, NCH_2CH$(CH_3)_2$), 2.35 (mc, 2H; cod CH_2 + NCH$_2$C*H*$(CH_3)_2$), 2.22 (mc, 1H; cod CH_2), 2.14 (mc, 2H; cod CH_2), 2.01 (mc, 2H; cod CH_2), 1.72 (mc, 1H; cod CH_2), 1.58 (mc, 1H; cod CH_2), 0.95 (d, ^3J(H,H) = 6.6 Hz, 9H, NCH$_2$CH(C$H_3)_2$), 0.81 (d, ^3J(H,H) = 6.6 Hz 9H, NCH$_2$CH(C$H_3)_2$), 0.75 (s, 9H; *t*Bu CH_3);

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 173.3 (N*C*N), 165.1 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.8 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.0 (imid *C*H), 120.8 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 84.9 (cod *C*H), 80.8 (cod *C*H), 73.1 (oxaz *C*H), 72.8 (oxaz *C*H_2), 64.5 (cod *C*H), 58.9 (cod *C*H), 58.1 (NCH_2CH$(CH_3)_2$), 46.9 (NCH_2), 34.1 (cod *C*H_2), 33.5 (*t*Bu *C*), 31.2 (NCH$_2$*C*H$(CH_3)_2$), 31.0 (cod *C*H_2), 30.0 (cod *C*H_2), 28.2 (cod *C*H_2), 25.1 (3C; *t*Bu *C*H_3), 19.9 (2C; NCH$_2$CH(*C*$H_3)_2$), 19.2 (2C; NCH$_2$CH(*C*$H_3)_2$);

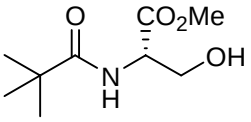
IR (KBr): $\tilde{\nu}$ = 2965w, 1680w, 1647w, 1609w, 1471w, 1419w, 1356m, 1279s, 1128bs, 971w, 889w, 838w, 713w, 676w cm^{-1};

MS (FAB): *m/z* (%): 564 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{55}H_{49}BF_{24}IrN_3O$ (1426.99): C 46.29, H 3.46, N 2.94; C 46.39, H 3.56, N 3.04

6.3.5 Synthesis of amides 85a,f,k

(*S*)-2-(2,2-dimethyl-propionylamino)-3-hydroxy-propionic acid methyl ester **85a**



A solution of (*S*)-serine methyl ester hydrochloride (6.00 g, 38.6 mmol) and triethylamine (11.7 g, 115.7 mmol) in CH_2Cl_2 (150 ml) was cooled down to -10°C under argon. Pivaloyl chloride (4.65 g; 38.6 mmol) was added dropwise over 5 minutes. The reaction mixture was stirred at room temperature for 12 hours then diluted with water (100 ml). The dichloromethane layer was separated, dried over magnesium sulfate and concentrated *in vacuo* to yield an yellow oil. The crude product was purified by chromatography on silica gel eluting with a mixture of AcOEt and hexane (4:1) to yield a colourless oil (5.90 g, 30.8 mmol, 80%).

$\boldsymbol{R_f}$ = 0.43 (AcOEt/Hex 4:1)

$[\alpha]_D^{20}$ = +24.6 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 6.61 (br, 1H; N*H*), 4.63 (mc, 1H; NHC*H*CO_2CH_3), 3.93 (mc, 2H; CH_2OH), 3.78 (s, 3H, CO_2CH_3), 2.68 (br, 1H, O*H*), 1.23 (s, 9H, $C(CH_3)_3$);

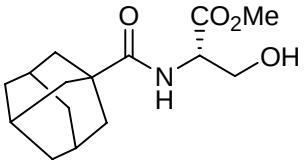
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 179.7 (N*C*O), 171.6 (CO_2CH_3), 64.1 (CH_2OH), 55.2 (NH*C*HCO_2), 53.2 (CO_2CH_3), 39.2 ($C(CH_3)_3$), 27.8 ($C(CH_3)_3$);

IR (NaCl): $\tilde{\nu}$ = 3396sbr, 2960s, 2878m, 1744s, 1645s, 1521s, 1438m, 1368m, 1204s, 1081m, 979w, 938w, 857w cm^{-1};

MS (FAB): *m/z* (%): 204 (100) $[M + H]^+$, 57 (66);

EA calcd (%) for $C_9H_{17}NO_4$ (203.24): C 53.19, H 8.43, N 6.89; found: C 52.88, H 8.54, N 7.00.

(*S*)-2-[(adamantane-1-carbonyl)-amino]-3-hydroxy-propionic acid methyl ester **85f**



Synthesis according to the previous general procedure using 1-adamantanecarbonylchloride (10.0 g, 50.3 mmol), (*S*)-serine methyl ester hydrochloride (7.83 g, 50.3 mmol) and triethylamine (15.3 g, 151 mmol) yielded a white solid (13.1 g, 93%, 46.8 mmol).

$\boldsymbol{R_f}$ = 0.59 (AcOEt/Hexane 1 :1);

m.p. 102-103°C; $[\alpha]_D^{20}$ = +21.8 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 6.59 (br, 1H; N*H*), 4.64 (mc, 1H; NHC*H*CO_2CH_3), 3.92 (mc, 2H; CH_2OH), 3.78 (s, 3H, CO_2CH_3), 2.76 (br, 1H, O*H*), 2.05 (mc, 3H; adam C*H*), 1.89 (mc, 6H; adam CH_2), 1.71 (mc, 6H; adam CH_2);

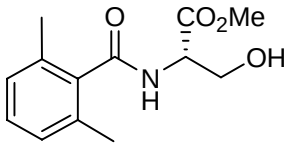
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 179.2 (N*C*O), 171.6 (*C*O_2CH_3), 64.2 (*C*H_2OH), 55.1 (NH*C*HCO_2), 53.2 (CO_2CH_3), 41.1 (adam *C*), 39.5 (adam *C*H_2), 36.8 (adam *C*H_2), 28.4 (adam *C*H);

IR (KBr): $\tilde{\nu}$ = 3446mbr, 3326mbr, 2902s, 1761s, 1622s, 1540s, 1451m, 1401w, 1344m, 1208m, 1071m, 975w, 647w cm^{-1};

MS (FAB): *m/z* (%): 282 (100) $[M + H]^+$, 135 (58);

EA calcd (%) for $C_{15}H_{23}NO_4$ (281.35): C 64.04, H 8.24, N 4.98; found: C 64.14, H 8.30, N 4.90.

(*S*)-3-hydroxy-2-(2,4,6-trimethyl-benzoylamino)-propionic acid methyl ester **85k**



Synthesis according to the previous general procedure using 2,6-dimethylbenzoylchloride (10.0 g, 59.4 mmol), (*S*)-serine methyl ester hydrochloride (9.24 g, 59.4 mmol) and triethylamine (18.0 g, 178 mmol) yielded a white solid (12.9 g, 86%, 51.1 mmol).

$\boldsymbol{R_f}$ = 0.55 (AcOEt/Hexane 4 :1);

m.p. 110-111°C;

$[\alpha]_D^{20}$ = +3.2 (c = 0.50, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.16 (t, ^3J(H,H) = 7.6 Hz, 1H; arom C*H*), 7.01 (d, ^3J(H,H) = 7.6 Hz, 2H; arom C*H*), 6.67 (br, 1H; N*H*), 4.84 (mc, 1H; NHC*H*CO_2CH_3), 4.06 (mc, 1H; C*H*$_2$OH), 3.95 (mc, 1H; C*H*$_2$OH), 3.79 (s, 3H; CO_2CH_3), 2.68 (br, 1H; O*H*), 2.32 (s, 6H, CCH_3);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 171.1 (CO_2CH_3), 137.0 (arom *C*CN), 134.7 (2C; arom *C*CH_3), 129.4 (arom *C*H), 127.9 (2C; arom *C*H), 63.7 (CH_2OH), 54.8 (NH*C*HCO_2), 53.1 (CO_2CH_3), 19.5 (2C; CCH_3), 1 quat. C not detected;

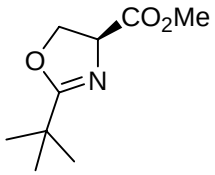
IR (KBr): $\tilde{\nu}$ = 3289sbr, 2957w, 2856w, 1741m, 1635.2s, 1545m, 1231m, 1161m, 1070m, 984w, 778m, 637m cm^{-1};

MS (FAB): *m/z* (%): 252 (46) $[M + H]^+$, 133 (100);

EA calcd (%) for $C_{13}H_{17}NO_4$ (251.29): C 62.14, H 6.82, N 5.57, O 25.47; found: C 61.98, H 6.77, N 5.64, O 25.61.

6.3.6 Synthesis of esters 86a,f,k

(*S*)-2-*tert*-butyl-4,5-dihydro-oxazole-4-carboxylic acid methyl ester **86a**



A solution of amide **85a** (2.40 g, 12.6 mmol) and methyl-*N*-triethylammoniosulfonyl-carbamate (3.29 g, 13.8 mmol) in THF (40 ml) was refluxed for 12 hours. The reaction mixture was concentrated *in vacuo* and the residue was diluted in dichloromethane. The organic layer was extracted three times with water, dried over magnesium sulfate in concentrated *in vacuo* to give an oil. The crude product was purified by distillation to yield a colourless oil (1.51 g, 8.2 mmol, 65%).

b.p. 45°C at 0.08 mbar;

$[\alpha]_D^{20}$ = +150.9 (c = 0.94, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 4.67 (mc, 1H; oxaz C*H*), 4.42 (mc, 1H; oxaz C*H*$_2$), 4.34 (mc, 1H; oxaz C*H*$_2$), 3.74 (s, 3H; CO_2CH_3), 1.20 (s, 9H, $C(CH_3)_3$);

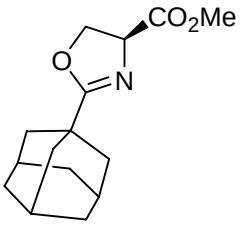
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 177.3 (N*C*O), 172.3 (CO_2CH_3), 69.8 (oxaz *C*H$_2$), 68.5 (oxaz *C*H), 52.9 (CO_2CH_3), 33.8 ($C(CH_3)_3$), 28.1 ($C(CH_3)_3$);

IR (NaCl): $\tilde{\nu}$ = 2975s, 1742s, 1651s, 1482m, 1438m, 1396w, 1363m, 1300m, 1144s,1061w, 981m, 785w, 728w cm^{-1};

MS (FAB): *m/z* (%): 186 (100) $[M + H]^+$;

EA calcd (%) for $C_9H_{15}NO_3$ (185.22): C 58.36, H 8.16, N 7.56; found: C 58.17, H 7.98, N 7.61.

(*S*)-2-adamantan-1-yl-4,5-dihydro-oxazole-4-carboxylic acid methyl ester **86f**



Synthesis according to the previous general procedure using amide **85f** (12.0 g, 42.6 mmol) and methyl-*N*-triethylammoniosulfonyl-carbamate (11.2 g, 46.9 mmol) yielded a colourless oil (8.07 g, 72%, 51.1 mmol).

$\boldsymbol{R_f}$ = 0.59 (AcOEt/Hexane, 1 :1);

$[\alpha]_D^{20}$ = +93.4 (c = 1.20, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 4.69 (mc, 1H; oxaz C*H*), 4.42 (mc, 1H; oxaz CH_2), 4.34 (mc, 1H; oxaz CH_2), 3.80 (s, 3H; CO_2CH_3), 2.04 (mc, 3H; adam C*H*), 1.94 (mc, 6H; adam CH_2), 1.74 (mc, 6H; adam CH_2);

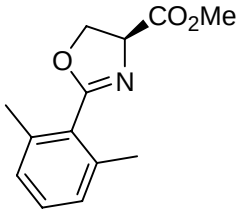
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 176.7 (N*C*O), 172.4 (CO_2CH_3), 69.4 (oxaz *C*H$_2$), 68.3 (oxaz *C*H), 52.9 (CO_2CH_3), 39.8 (adam *C*H$_2$), 36.9 (adam *C*H$_2$), 35.8 (adam *C*), 28.3 (adam *C*H);

IR (NaCl): $\tilde{\nu}$ = 2906s, 2851m, 1744s, 1648m, 1452m, 1351w, 1275w, 1208m, 1056m, 970w cm^{-1};

MS (FAB): *m/z* (%): 264 (100) $[M + H]^+$;

EA calcd (%) for $C_{15}H_{21}NO_3$ (263.33): C 68.42, H 8.04, N 5.32; found: C 68.46, H 7.82, N 5.21.

(*S*)-2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazole-4-carboxylic acid methyl ester **86k**



Synthesis according to the previous general procedure using amide **85k** (10.0 g, 39.8 mmol) and methyl-*N*-triethylammoniosulfonyl-carbamate (10.4 g, 43.7 mmol) yielded a colourless oil (6.53 g, 70%, 28.0 mmol).

$\boldsymbol{R_f}$ = 0.65 (AcOEt/Hexane 4 :1);

$[\alpha]_D^{20}$ = +95.4 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.19 (t, ^3J(H,H) = 7.6 Hz, 1H; arom C*H*), 7.03 (d, ^3J(H,H) = 7.6 Hz, 2H; arom C*H*), 4.99 (mc, 1H; oxaz C*H*), 4.67 (mc, 1H; oxaz CH_2), 4.55 (mc, 1H; oxaz CH_2), 3.82 (s, 3H; OCH_3), 2.33 (s, 6H, CCH_3);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 172.1 (*C*$O_2$$CH_3$), 167.5 (N*C*O), 137.5 (2C; arom *C*CH_3), 130.1 (arom *C*H), 128.3 (arom *C*CN), 127.8 (2C; arom *C*H), 69.7 (oxaz *C*H_2), 69.1 (oxaz *C*H), 53.1 (CO_2*C*H_3), 20.0 (2C; C*C*H_3);

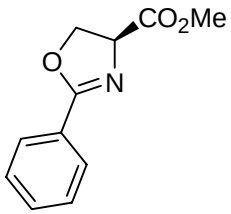
IR (NaCl): $\tilde{\nu}$ = 2956w, 1744s, 1656m, 1466w, 1352w, 1286w, 1207m, 1051w, 965w, 776w cm^{-1};

MS (FAB): *m/z* (%): 234 (100) $[M + H]^+$;

EA calcd (%) for $C_{13}H_{15}NO_3$ (233.27): C 66.94, H 6.48, N 6.00; found: C 66.55, H 6.47, N 6.21.

6.3.7 Synthesis of ester 86p

(*S*)-2-phenyl-4,5-dihydro-oxazole-4-carboxylic acid methyl ester **86p**



Ethyl benzimidate hydrochloride (5.00 g, 26.9 mmol) was dissolved in dichloromethane (100 ml). The solution was extracted three times with an aqueous solution of $NaHCO_3$ and concentrated *in vacuo* to yield an oil (3.77 g, 25.3 mmol). The oil was diluted in 1,2-

dichlorethane (150 ml) and (*S*)-serine methyl ester hydrochloride (4.32 g, 27.8 mmol) was added. The suspension was refluxed for 20 hours then filtered and concentrated *in vacuo* to remove the solvent. The crude product was purified by chromatography on silica gel eluting with a mixture of AcOEt and hexane (3:1) to yield a colourless oil (5.02 g, 24.5 mmol, 91%).

$\boldsymbol{R_f}$ = 0.57 (AcOEt/Hex 3:1)

$[\alpha]_D^{20}$ = +99.3 (c = 1.36, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.97 (mc, 2H; arom C*H*), 7.49 (mc, 1H; arom C*H*), 7.40 (mc, 2H; arom C*H*), 4.95 (mc, 1H; oxaz C*H*), 4.69 (mc, 1H; oxaz CH_2), 4.59 (mc, 1H; oxaz CH_2), 3.81 (s, 3H, OCH_3);

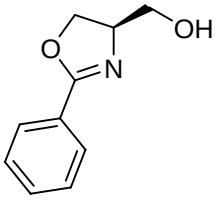
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 172.0 (*C*O_2CH_3), 166.7 (N*C*O), 132.3 (arom *C*H), 129.0 (2C; arom *C*H), 128.8 (2C; arom *C*H), 127.3 (arom, *C*), 70.0 (oxaz *C*H_2), 69.0 (oxaz *C*H), 53.1 (CO_2*C*H_3);

IR (NaCl): $\tilde{\nu}$ = 2953w, 1742s, 1642m, 1450w, 1362m, 1210m, 1090m, 1026w, 971w, 779w, 697m cm^{-1}; MS (FAB): *m/z* (%): 206 (100) $[M + H]^+$;

EA calcd (%) for $C_{11}H_{11}NO_3$ (205.21): C 64.38, H 5.40, N 6.83; found: C 64.26, H 5.66, N 7.06.

6.3.8 Synthesis of oxazoline alcohols 87p,a,f,k

(*R*)-(2-Phenyl-4,5-dihydro-oxazol-4-yl)-methanol **87p**



Ester **86p** (11.0 g, 53.9 mmol) and 300 ml of dried THF were added under argon to a 2L round bottom flask equipped with a thermometer and an addition funnel. A solution of DIBAL in THF (170 ml, 1.0 mmol/ml) was added dropwise at -10°C. The reaction mixture was stirred overnight at room temperature. At the end of the reaction, a solution of Seignette's salt (400 ml, 20% w/w) was carefully added under stirring and the mixture was extracted three times with ethyl acetate. The combined organic layers were dried over magnesium sulfate and concentrated *in vacuo* to yield an yellow oil. The crude product was purified by chromatography on silica gel eluting with AcOEt to yield a white solid (6.4 g, 36.1 mmol, 67%).

R_f = 0.33 (AcOEt)

m.p. 99-100°C;

$[\alpha]_D^{20}$ = +89.0 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.97 (mc, 2H; arom C*H*), 7.42 (mc, 1H; arom C*H*), 7.31 (mc, 2H; arom C*H*), 4.30 – 4.50 (m, 3H; 2 x oxaz CH_2 + 1 x oxaz C*H*), 3.99 (mc, 1H; CH_2OH), 3.65 (mc, 1H; CH_2OH), 3.53 (br, 1H; OH);

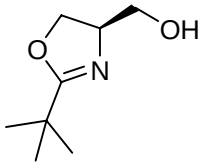
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 166.0 (N*C*O), 131.9 (arom *C*H), 128.7 (2C; arom *C*H), 128.6 (2C; arom *C*H), 127.5 (arom, *C*), 69.5 (oxaz *C*H_2), 68.5 (oxaz *C*H), 64.1 (*C*H_2OH);

IR (KBr): $\tilde{\nu}$ = 3266sbr, 2928m, 1652s, 1500m, 1363m, 1276m, 1098m, 958m, 783w, 693m cm^{-1};

MS (FAB): *m/z* (%): 178 (100) $[M + H]^+$;

EA calcd (%) for $C_{10}H_{11}NO_2$ (177.20): C 67.78, H 6.26, N 7.90, O 18.06; found: C 67.60, H 6.28, N 7.87, O 17.80.

(*R*)-(2-tert-butyl-4,5-dihydro-oxazol-4-yl)-methanol **87a**



Synthesis according to the previous general procedure using ester **86a** (6.00 g, 32.4 mmol) and a solution of DIBAL in THF (100 ml, 1.0 mmol/ml) yielded a white solid (4.00 g, 78%, 25.4 mmol).

m.p. 37-38°C;

b.p. 62°C at 0.1 mbar;

$[\alpha]_D^{20}$ = +93.4 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 4.30 (mc, 1H; oxaz CH_2), 4.21 (mc, 1H; oxaz C*H*), 4.09 (mc, 1H; oxaz CH_2), 3.78 (mc, 1H; CH_2OH), 3.54 (mc, 1H; CH_2OH), 2.66 (br, 1H; OH), 1.22 (s, 9H, C(CH_3)$_3$);

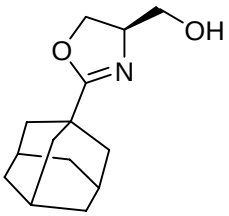
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 176.8 (N*C*O), 69.8 (oxaz *C*H_2), 67.7 (oxaz *C*H), 64.7 (*C*H_2OH), 33.8 (*C*(CH_3)$_3$), 28.3 (C(*C*H_3)$_3$);

IR (KBr): $\tilde{\nu}$ = 3228sbr, 2960s, 1648s, 1459m, 1226w, 1148m, 970m, 904w, 816w cm^{-1};

MS (FAB): *m/z* (%): 158 (100) $[M + H]^+$, 57 (63), 43 (35), 41 (35);

EA calcd (%) for $C_8H_{15}NO_2$ (157.21): C 61.12, H 9.62, N 8.91; found: C 60.71, H 9.83, N 8.74.

(*R*)-(2-adamantan-1-yl-4,5-dihydro-oxazol-4-yl)-methanol **87f**



Synthesis according to the previous general procedure using ester **86f** (7.50 g, 28.5 mmol) and a solution of DIBAL in THF (88 ml, 1.0 mmol/ml) yielded a white solid (4.26 g, 63%, 18.1 mmol).

$\boldsymbol{R_f}$ = 0.21 (AcOEt);

m.p. 104-105°C; $[\alpha]_D^{20}$ = +66.7 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 4.28 (mc, 1H; oxaz CH_2), 4.21 (mc, 1H; oxaz C*H*), 4.08 (mc, 1H; oxaz CH_2), 3.79 (mc, 1H; CH_2OH), 3.53 (mc, 1H; CH_2OH), 2.68 (br, 1H; OH), 2.01 (mc, 3H; adam C*H*), 1.89 (mc, 6H; adam CH_2), 1.71 (mc, 6H; adam CH_2);

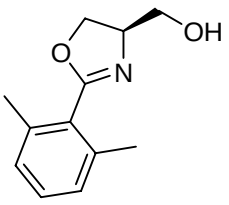
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 176.5 (N*C*O), 69.5 (oxaz *C*H_2), 67.3 (oxaz *C*H), 64.6 (*C*H_2OH), 40.0 (adam *C*H_2), 36.9 (adam *C*H_2), 35.9 (adam *C*), 28.3 (adam *C*H);

IR (KBr): $\tilde{\nu}$ = 3222sbr, 2907s, 1648s, 2848s, 1651s, 1473w, 1452m, 1354m, 1268w, 1230m, 1059m, 813w, 608w cm^{-1};

MS (FAB): *m/z* (%): 236 (100) $[M + H]^+$;

EA calcd (%) for $C_{14}H_{21}NO_2$ (235.32): C 71.46, H 8.99, N 5.95; found: C 71.09, H 8.81, N 5.72.

(*R*)-[2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazol-4-yl]-methanol **87k**



Synthesis according to the previous general procedure using ester **86k** (6.50 g, 27.9 mmol) and a solution of DIBAL in THF (87 ml, 1.0 mmol/ml) yielded a white solid (3.00 g, 52%, 14.0 mmol).

R_f = 0.17 (AcOEt/Hexane 2 :1);

m.p. 104-105°C;

$[\alpha]_D^{20}$ = +66.0 (c = 0.50, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.19 (t, ^3J(H,H) = 7.6 Hz, 1H; arom C*H*), 7.04 (d, ^3J(H,H) = 7.6 Hz, 2H; arom C*H*), 4.46 (mc, 2H; oxaz CH_2), 4.24 (mc, 1H; oxaz C*H*), 3.87 (mc, 1H; CH_2OH), 3.65 (mc, 1H; CH_2OH), 2.85 (br, 1H; OH), 2.30 (s, 6H, CCH_3);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 166.4 (N*C*O), 137.2 (2C; arom *C*CH_3), 129.9 (arom *C*H), 129.0 (arom *C*CN), 127.8 (2C; arom *C*H), 69.5 (oxaz *C*H_2), 68.7 (oxaz *C*H), 64.6 (*C*H_2OH), 20.1 (2C; C*C*H_3);

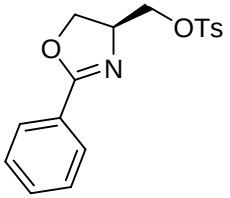
IR (KBr): $\tilde{\nu}$ = 3210mbr, 2925m, 1663s, 1594w, 1467m, 1349m, 1299w, 1261m, 1107m, 1054m, 940m, 701w cm^{-1};

MS (FAB): *m/z* (%): 206 (100) $[M + H]^+$;

EA calcd (%) for $C_{12}H_{15}NO_2$ (205.25): C 70.22, H 7.37, N 6.82; found: C 70.10, H 7.31, N 6.68.

6.3.9 Synthesis of tosylates 88p,a,f,k

(*S*)-toluene-4-sulfonic acid 2-phenyl-4,5-dihydro-oxazol-4-ylmethyl ester **88p**



Triethylamine (3.98 g, 39.4 mmol) was added dropwise to a solution of alcohol **87p** (6.35 g, 35.8 mmol) and tosyl chloride (13.65 g, 71.6 mmol) in dichloromethane (40 ml). The reaction mixture was stirred at room temperature for 8 hours then concentrated *in vacuo* to remove the solvent. The crude product was purified by chromatography on silica gel eluting with a mixture of AcOEt and hexane (from 3:7 to 7:3) to yield a colourless oil which crystallised on standing (8.41 g, 25.4 mmol, 71%).

R_f = 0.48 (AcOEt/Hexane 1 :1);

m.p. 109-110°C;

$[\alpha]_D^{20}$ = +96.5 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.86 (mc, 2H; tos C*H*), 7.77 (mc, 2H; tos C*H*), 7.49 (mc, 1H; arom C*H*), 7.40 (mc, 2H; arom C*H*), 7.30 (mc, 2H; arom C*H*), 4.49 (mc, 2H;

oxaz C*H* + oxaz CH_2), 4.34 (mc, 1H; oxaz CH_2), 4.27 (mc, 1H; CH_2OH), 4.04 (mc, CH_2OH), 2.43 (s, 3H; tos CH_3);

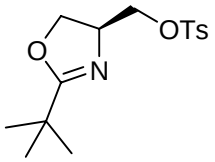
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 145.4 (tos *C*), 132.9 (tos *C*), 132.3 (arom *C*H), 130.3 (2C, tos *C*H), 128.8 (2C; arom *C*H), 128.8 (2C; arom *C*H), 128.4 (2C, tos *C*H), 127.3 (arom, *C*), 71.1 (*C*H_2), 70.3 (*C*H_2), 65.4 (oxaz *C*H), 22.1 (tos *C*H_3), 1 quat. C not detected;

IR (NaCl): $\tilde{\nu}$ = 2976w, 1648m, 1452w, 1366s, 1269w,1176s, 1023m, 969m, 837m, 690m, 555m cm^{-1};

MS (FAB): *m/z* (%): 332 (100) $[M + H]^+$;

EA calcd (%) for $C_{17}H_{17}NO_4S$ (331.39): C 61.61, H 5.17, N 4.23, O 19.31; found: C 61.56, H 5.20, N 4.19, O 19.50.

(*S*)-toluene-4-sulfonic acid 2-tert-butyl-4,5-dihydro-oxazol-4-ylmethyl ester **88a**



Synthesis according to the previous general procedure using alcohol **87a** (2.00 g, 12.6 mmol), tosyl chloride (4.82 g, 25.3 mmol) and triethylamine (1.28 g, 12.6 mmol) yielded a white solid (2.83 g, 72%, 9.10 mmol).

R_f = 0.54 (AcOEt/Hexane 1 :1);

m.p. 63-64°C;

$[\alpha]_D^{20}$ = +81.3 (c = 1.44, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.77 (mc, 2H; arom C*H*), 7.34 (mc, 2H; arom C*H*), 4.26 (mc, 2H; oxaz C*H* + oxaz CH_2), 4.14 (mc, 2H; oxaz CH_2 + CH_2OH), 3.91 (mc, 1H; CH_2OH), 2.44 (s, 3H; tos CH_3), 1.16 (s, 9H, C(CH_3)$_3$);

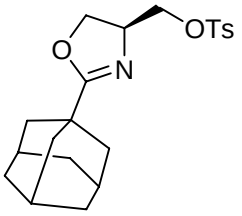
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 145.4 (arom *C*), 133.0 (arom *C*), 130.3 (2C, arom *C*H), 128.4 (2C, arom *C*H), 71.2 (*C*H_2), 70.2 (*C*H_2), 64.7 (oxaz *C*H), 33.7 (*C*(CH$_3$)$_3$), 28.1 (C(*C*H$_3$)$_3$), 22.1 (tos *C*H$_3$), 1 quat. C not detected;

IR (KBr): $\tilde{\nu}$ = 2980m, 1735w, 1658s, 1598m, 1481m, 1360s, 1284w, 1180s, 1175s, 1027w, 947s, 706w, 668s, 555s cm^{-1};

MS (FAB): *m/z* (%): 312 (64) $[M + H]^+$, 57 (100), 41 (36);

EA calcd (%) for $C_{15}H_{21}NO_4S$ (311.40): C 57.86, H 6.80, N 4.50, O 20.55; found: C 57.88, H 6.84, N 4.44, O 20.47.

(*S*)-toluene-4-sulfonic acid 2-adamantan-1-yl-4,5-dihydro-oxazol-4-ylmethyl ester **88f**



Synthesis according to the previous general procedure using alcohol **87f** (3.80 g, 16.1 mmol), tosyl chloride (6.15 g, 32.3 mmol) and triethylamine (1.63 g, 16.1 mmol) yielded a colourless oil (5.20 g, 83%, 13.3 mmol).

$\boldsymbol{R_f}$ = 0.52 (AcOEt/Hexane 1 :1);

$[\alpha]_D^{20}$ = +58.8 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.77 (mc, 2H; arom C*H*), 7.34 (mc, 2H; arom C*H*), 4.23 (mc, 2H; oxaz C*H* + oxaz CH_2), (4.12 mc, 2H; oxaz CH_2 + CH_2O), 3.92 (mc, 1H; CH_2OH), 2.44 (s, 3H; tos CH_3), 1.98 (mc, 3H; adam C*H*), 1.81 (mc, 6H; adam CH_2), 1.69 (mc, 6H; adam CH_2);

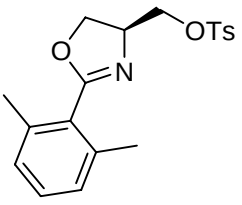
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 145.4 (arom *C*), 133.0 (arom *C*), 130.3 (2C, arom *C*H), 128.4 (2C, arom *C*H), 71.2 (*C*H_2), 69.9 (*C*H_2), 64.3 (oxaz *C*H), 39.8 (adam *C*H_2), 36.8 (adam *C*H_2), 35.8 (adam *C*), 28.2 (adam *C*H), 22.1 (tos *C*H_3), 1 quat. C not detected;

IR (NaCl): $\tilde{\nu}$ = 2905s, 2852w, 1650m, 1453m, 1370m, 1227w, 1177s, 1055w, 971m, 813.5w, 665m cm^{-1};

MS (FAB): *m/z* (%): 390 (100) $[M + H]^+$;

EA calcd (%) for $C_{21}H_{27}NO_4S$ (389.51): C 64.75, H 6.99, N 3.60; found: C 64.76, H 7.19, N 3.48.

(*S*)-toluene-4-sulfonic acid 2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazol-4-ylmethyl ester **88k**



Synthesis according to the previous general procedure using alcohol **87k** (2.65 g, 12.9 mmol), tosyl chloride (4.92 g, 25.8 mmol) and triethylamine (1.31 g, 12.9 mmol) yielded a colourless oil (2.30 g, 50%, 6.40 mmol).

$\boldsymbol{R_f}$ = 0.49 (AcOEt/Hexane 1 :1);

$[\alpha]_D^{20}$ = +69.2 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.80 (mc, 2H; tos C*H*), 7.34 (mc, 2H; tos C*H*), 7.49 (mc, 1H; arom C*H*), 7.17 (t, ^3J(H,H) = 7.6 Hz, 1H; arom C*H*), 7.01 (d, ^3J(H,H) = 7.6 Hz, 2H; arom C*H*), 4.57 (mc, 1H; oxaz C*H*), 4.44 (mc, 1H; oxaz CH_2), 4.32 (mc, 1H; oxaz CH_2), 4.26 (mc, 1H; CH_2OH), 4.13 (mc, 1H; CH_2OH), 2.44 (s, 3H; tos CH_3), 2.26 (s, 6H, CCH_3);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 167.0 (N*C*O), 145.6 (tos *C*), 137.3 (2C; arom *C*CH_3), 132.9 (tos *C*), 130.4 (2C, tos *C*H), 130.0 (arom *C*H), 128.6 (arom *C*CN), 128.4 (2C, tos *C*H), 127.8 (2C; arom *C*H), 70.7 (oxaz *C*H_2), 69.3 (*C*H_2OH), 65.8 (oxaz *C*H), 22.1 (tos *C*H_3), 20.1 (2C; C*C*H_3);

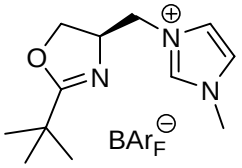
IR (NaCl): $\tilde{\nu}$ = 2962w, 2922w, 1662m, 1596w, 1464w, 1360s, 1179s, 1096m, 1046m, 957m, 818m, 777m, 666m cm^{-1};

MS (FAB): *m/z* (%): 360 (100) $[M + H]^+$;

EA calcd (%) for $C_{19}H_{21}NO_4S$ (359.44): C 63.49, H 5.89, N 3.90; found: C 63.36, H 5.98, N 3.88.

6.3.10 Synthesis of imidazolium salts 89a-p

(*R*)-1-(2-*tert*-butyl-4,5-dihydro-oxazol-4-ylmethyl)-3-methyl-3*H*-imidazol-1-ium **89a**



A solution of tosylate **88a** (400 mg, 1.28 mmol) and 1-methyl-1*H*-imidazole (105 mg, 1.28 mmol) in DMF (0.5 ml) was heated at 80°C for 8 hours. The reaction mixture was concentrated *in vacuo* at 80°C and the residue was diluted in acetone (5 ml). $NaBAr_F$ (1.13 g, 1.28 mmol) was added to the solution which was stirred at room temperature for 30 minutes. The reaction mixture was filtered and concentrated *in vacuo* to remove the solvent. The crude product was purified by chromatography on a plug of silica gel eluting with CH_2Cl_2 (1L) to yield a white solid (1.06 g, 0.973 mmol, 76%).

m.p. 120-121°C;

$[\alpha]_D^{20}$ = +35.5 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.45 (s, 1H; NC*H*N), 7.69 (mc, 8H; BAr_F *ortho* C*H*), 7.52 (mc, 4H; BAr_F para C*H*), 7.07 (mc, 1H; imid C*H*), 6.92 (mc, 1H; imid C*H*), 4.40 (mc, 1H; oxaz CH_2), 4.30 (mc, 1H; oxaz C*H*), 4.05 (mc, 1H; NCH_2), 3.81 (mc, 2H; oxaz CH_2 + NCH_2), 3.72 (s, 3H, NCH_3), 1.16 (s, 9H; *t*Bu CH_3);

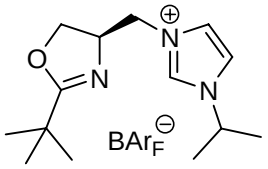
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 178.0 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 135.3 (N*C*HN), 134.7 (br, 8C; BAr_F *ortho C*H), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.7 (imid *C*H), 122.9 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 69.2 (oxaz *C*H_2), 64.7 (oxaz *C*H), 54.1 (N*C*H_2), 36.5 (N*C*H_3), 33.5 (*t*Bu *C*), 27.4 (3C; *t*Bu *C*H_3);

IR (KBr): $\tilde{\nu}$ = 3163w, 3098w, 2980w, 1655w, 1610w, 1577w, 1562w, 1482w, 1356m, 1282s, 1122sbr, 932w, 889w, 839w, 745w, 713w, 682w, 671w, 624w cm^{-1};

MS (FAB): *m/z* (%): 222 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{44}H_{32}BF_{24}N_3O$ (1085.52): C 48.68, H 2.97, N 3.87; found: C 48.63, H 3.15, N 3.64.

(*R*)-1-(2-*tert*-butyl-4,5-dihydro-oxazol-4-ylmethyl)-3-isopropyl-3*H*-imidazol-1-ium **89b**



Synthesis according to the previous general procedure using tosylate **88a** (400 mg, 1.28 mmol), isopropylimidazole (141 mg, 1.28 mmol) and $NaBAr_F$ (1.13 g, 1.28 mmol) yielded a white solid (1.03 g, 72%, 0.922 mmol).

m.p. 63-64°C;

$[\alpha]_D^{20}$ = +32.1 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.56 (s, 1H; NC*H*N), 7.69 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.08 (mc, 2H; imid C*H*), 4.40 (mc, 2H; oxaz CH_2 + *i*Pr C*H*), 4.32 (mc, 1H; oxaz C*H*), 4.08 (mc, 1H; NCH_2), 3.85-3.75 (m, 2H; oxaz CH_2 + NCH_2), 3.72 (mc, 6H, *i*Pr CH_3), 1.16 (s, 9H; *t*Bu CH_3);

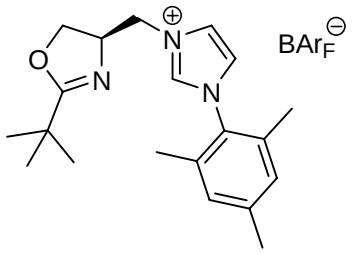
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 178.1 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.7 (br, 8C; BAr_F *ortho C*H), 133.3 (N*C*HN), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.6 (imid *C*H), 120.0 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 69.2 (oxaz *C*H_2), 64.6 (oxaz *C*H), 54.2 (N*C*H_2), 54.0 (*i*Pr *C*H), 33.4 (*t*Bu *C*), 27.4 (3C; *t*Bu *C*H_3), 22.4 (*i*Pr *C*H_3), 22.4 (*i*Pr *C*H_3);

IR (KBr): $\tilde{\nu}$ = 3172w, 2981w, 1651w, 1611w, 1585w, 1552w, 1466w, 1356m, 1282s, 1121sbr, 987w, 936w, 905w, 889w, 839w, 737w, 714w, 682w, 671w, 652w cm^{-1};

MS (FAB): *m/z* (%): 250 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{46}H_{36}BF_{24}N_3O$ (1113.26): C 49.62, H 3.26, N 3.77; found: C 49.88, H 3.21, N 3.49.

(*R*)-1-(2-*tert*-butyl-4,5-dihydro-oxazol-4-ylmethyl)-3-(2,4,6-trimethyl-phenyl)-3*H*-imidazol-1-ium **89c**



Synthesis according to the previous general procedure using tosylate **88a** (400 mg, 1.28 mmol), mesitylimidazole (239 mg, 1.28 mmol) and $NaBAr_F$ (1.13 g, 1.28 mmol) yielded a white solid (1.20 g, 78%, 1.00 mmol).

m.p. 142-143°C;

$[\alpha]_D^{20}$ = +19.8 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.48 (s, 1H; NC*H*N), 7.69 (mc, 8H; BAr_F *ortho* C*H*), 7.51 (mc, 4H; BAr_F para C*H*), 7.31 (mc, 1H; imid C*H*), 7.15 (mc, 1H; imid C*H*), 7.03 (mc, 2H; arom C*H*), 4.39 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.21 (mc, 1H; NCH_2), 3.96 (mc, 1H; NCH_2), 3.83 (mc, 1H; oxaz CH_2), 2.33 (s, 3H, $C_{arom}CH_3$), 1.96 (br, 3H, $C_{arom}CH_3$), 1.93 (br, 3H, $C_{arom}CH_3$), 1.15 (s, 9H; *t*Bu CH_3);

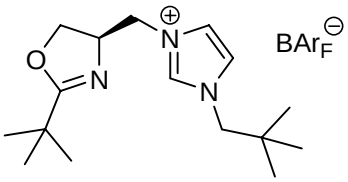
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 177.9 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 142.6 (arom *C*), 136.0 (N*C*HN), 134.7 (br, 8C; BAr_F *ortho C*H), 133.9 (arom *C*), 133.7 (arom *C*), 130.2 (arom *C*H), 130.1 (arom *C*H), 129.8 (arom *C*), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.9 (imid *C*H), 123.4 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 69.1 (oxaz *C*H_2), 64.9 (oxaz *C*H), 54.4 (N*C*H_2), 33.4 (*t*Bu *C*), 27.5 (3C; *t*Bu *C*H_3), 21.0 ($C_{arom}CH_3$), 16.8 ($C_{arom}CH_3$), 16.9 ($C_{arom}CH_3$);

IR (KBr): $\tilde{\nu}$ = 3161w, 2978w, 1654w, 1610w, 1560w, 1482w, 1355m, 1278s, 1121sbr, 931w, 887w, 839w, 744w, 713w, 682w, 670w, 624w, 577 cm^{-1};

MS (FAB): *m/z* (%): 326 (100) $[M - BAr_F]^+$;

EA calcd (%) for $C_{52}H_{40}BF_{24}N_3O$ (1189.67): C 52.50, H 3.39, N 3.53; found: C 52.06, H 3.46, N 3.34.

(*R*)-1-(2-*tert*-butyl-4,5-dihydro-oxazol-4-ylmethyl)-3-(2,2-dimethyl-propyl)-3*H*-imidazol-1-ium **89d**



Synthesis according to the previous general procedure using tosylate **88a** (400 mg, 1.28 mmol), neopentylimidazole (177 mg, 1.28 mmol) and $NaBAr_F$ (1.13 g, 1.28 mmol) yielded a colourless oil (1.00 g, 68%, 0.870 mmol).

$[\alpha]_D^{20}$ = +26.2 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.48 (s, 1H; NC*H*N), 7.68 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.01 (mc, 1H; imid C*H*), 6.95 (mc, 1H; imid C*H*), 4.42 (mc, 1H; oxaz CH_2), 4.31 (mc, 1H; oxaz C*H*), 4.07 (mc, 1H; NCH_2), 3.85-3.75 (m, 4H; oxaz CH_2 + NCH_2 + NCH_2C(CH_3)$_3$), 1.17 (s, 9H; *t*Bu CH_3), 0.93 (s, 9H; $NCH_2C(CH_3)_3$);

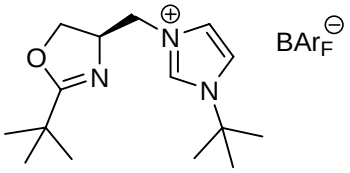
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 135.5 (N*C*HN), 134.7 (br, 8C; BAr_F *ortho C*H), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.4 (imid *C*H), 122.6 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 69.3 (oxaz *C*H_2), 64.6 (oxaz *C*H), 62.4 (N*C*H_2C(CH_3)$_3$), 54.0 (N*C*H_2), 32.5 (*t*Bu *C*), 27.4 (3C; *t*Bu *C*H_3), 26.6 (3C; $NCH_2C(CH_3)_3$), 2 quat. C not detected;

IR (NaCl): $\tilde{\nu}$ = 3174w, 2979w, 1648w, 1610w, 1590w, 1560w, 1482w, 1358m, 1281s, 1120sbr, 986w, 935w, 905w, 889w, 839w, 738w, 714w, 682w, 670w, 628w cm^{-1};

MS (FAB): *m/z* (%): 278 (100) $[M - BAr_F]^+$;

EA calcd (%) for $C_{48}H_{40}BF_{24}N_3O$ (1141.62): C 50.50, H 3.53, N 3.68; found: C 49.63, H 3.37, N 3.46.

(*R*)-3-*tert*-butyl-1-(2-*tert*-butyl-4,5-dihydro-oxazol-4-ylmethyl)-3*H*-imidazol-1-ium **89e**



Synthesis according to the previous general procedure using tosylate **88a** (400 mg, 1.28 mmol), *tert*-butylimidazole (160 mg, 1.28 mmol) and $NaBAr_F$ (1.13 g, 1.28 mmol) yielded of a white solid (1.08 g, 75%, 0.960 mmol).

m.p. 84-85°C;

$[\alpha]_D^{20}$ = +35.1 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.65 (s, 1H; NC*H*N), 7.69 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.17 (mc, 1H; imid C*H*), 7.07 (mc, 1H; imid C*H*), 4.40 (mc, 1H; oxaz CH_2), 4.32 (mc, 1H; oxaz C*H*), 4.08 (mc, 1H; NCH_2), 3.82 (mc, 2H; oxaz CH_2 + NCH_2), 1.55 (s, 9H; *t*Bu_{imid} CH_3), 1.17 (s, 9H; *t*Bu_{oxaz} CH_3);

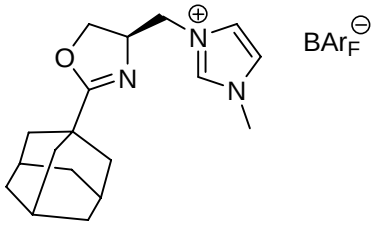
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 178.0 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.7 (br, 8C; BAr_F *ortho C*H), 133.0 (N*C*HN), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.5 (imid *C*H), 119.4 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 69.2 (oxaz *C*H_2), 64.6 (oxaz *C*H), 61.1 (*t*Bu_{imid} *C*), 53.9 (N*C*H_2), 33.4 (*t*Bu_{oxaz} *C*), 29.4 (3C; *t*Bu_{imid} *C*H_3), 27.4 (3C; *t*Bu_{oxaz} *C*H_3);

IR (KBr): $\tilde{\nu}$ = 3176w, 2981w, 1652w, 1611w, 1581w, 1550w, 1546w, 1466w, 1357m, 1281s, 1120sbr, 986w, 936w, 901w, 889w, 839w, 737w, 714w, 682w, 670w, 656w cm^{-1};

MS (FAB): *m/z* (%): 264 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{47}H_{38}BF_{24}N_3O$ (1127.51): C 50.06, H 3.31, N 3.73; found: C 49.99, H 3.33, N 3.51.

(*R*)-1-(2-adamantan-1-yl-4,5-dihydro-oxazol-4-ylmethyl)-3-methyl-3*H*-imidazol-1-ium **89f**



Synthesis according to the previous general procedure using tosylate **88f** (400 mg, 1.03 mmol), methylimidazole (84 mg, 1.03 mmol) and $NaBAr_F$ (913 mg, 1.03 mmol) yielded a white solid (778 mg, 65%, 0.670 mmol).

m.p. 142-143°C;

$[\alpha]_D^{20}$ = +29.5 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.48 (s, 1H; NC*H*N), 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.08 (mc, 1H; imid C*H*), 6.92 (mc, 1H; imid C*H*), 4.37 (mc, 1H; oxaz CH_2), 4.30 (mc, 1H; oxaz C*H*), 4.06 (mc, 1H; NCH_2), 3.82 (mc, 2H; oxaz CH_2 + NCH_2), 3.72 (s, 3H, NCH_3), 2.01 (mc, 3H; adam C*H*), 1.82 (mc, 6H; adam CH_2), 1.75 (mc, 3H; adam CH_2), 1.66 (mc, 3H; adam CH_2);

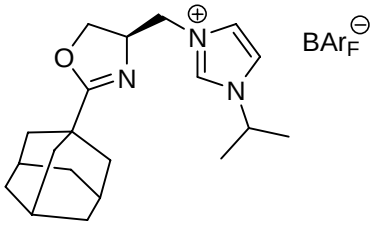
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 135.3 (NCHN), 134.7 (br, 8C; BAr_F *ortho* C*H*), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.7 (imid *C*H), 122.9 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 68.7 (oxaz *C*H_2), 64.4 (oxaz *C*H), 54.2 (N*C*H_2), 39.4 (adam *C*H_2), 36.5 (N*C*H_3), 36.2 (adam *C*H_2), 35.5 (adam *C*), 27.6 (adam *C*H), 1 C quat. not detected;

IR (KBr): $\tilde{\nu}$ = 2916w, 2862w, 1651w, 1612w, 1566w, 1458w, 1350m, 1272s, 1103sbr, 887w, 833w, 748w, 710w, 671w cm^{-1};

MS (FAB): *m/z* (%): 300 (100) $[M - BAr_F]^+$;

EA calcd (%) for $C_{50}H_{38}BF_{24}N_3O$ (1163.63): C 51.61, H 3.29, N 3.61; found: C 51.42, H 3.28, N 3.54.

(*R*)-1-(2-adamantan-1-yl-4,5-dihydro-oxazol-4-ylmethyl)-3-isopropyl-3*H*-imidazol-1-ium **89g**



Synthesis according to the previous general procedure using tosylate **88f** (400 mg, 1.03 mmol), isopropylimidazole (113 mg, 1.03 mmol) and $NaBAr_F$ (913 mg, 1.03 mmol) yielded a colourless oil (613 mg, 50%, 515 mmol).

$[\alpha]_D^{20}$ = +20.4 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.59 (s, 1H; NC*H*N), 7.73 (mc, 8H; BAr_F *ortho* C*H*), 7.56 (mc, 4H; BAr_F para C*H*), 7.12 (mc, 1H; imid C*H*), 7.10 (mc, 1H; imid C*H*), 4.50-4.25 (m, 3H; oxaz CH_2 + oxaz C*H* + *i*Pr C*H*), 4.11 (mc, 1H; NCH_2), 3.90-3.75 (m, 2H; oxaz CH_2 + NCH_2), 2.01 (mc, 3H; adam C*H*), 1.84 (mc, 6H; adam CH_2), 1.69 (mc, 3H; adam CH_2), 1.49 (mc, 3H; adam CH_2), 1.48 (mc, 6H; *i*Pr CH_3);

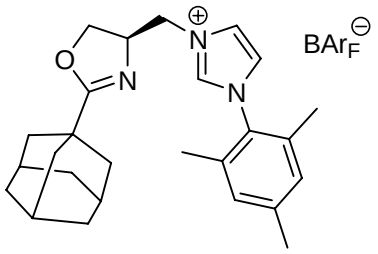
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 177.2 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.7 (br, 8C; BAr_F *ortho C*H), 133.3 (N*C*HN), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.6 (imid *C*H), 119.9 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 68.7 (oxaz *C*H_2), 64.5 (oxaz *C*H), 54.2 (N*C*H_2), 54.1 (*i*Pr *C*H), 39.4 (adam *C*H_2), 36.1 (adam *C*H_2), 35.4 (adam *C*), 27.7 (adam *C*H), 22.4 (*i*Pr *C*H_3), 22.3 (*i*Pr *C*H_3);

IR (NaCl): $\tilde{\nu}$ = 2908w, 2854w, 1643w, 1612w, 1558w, 1458w, 1350m, 1273s, 1111sbr, 975w, 933w, 887w, 833w, 741w, 710w, 671w cm^{-1};

MS (FAB): *m/z* (%): 328 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{52}H_{42}BF_{24}N_3O$ (1191.68): C 52.41, H 3.55, N 3.53; found: C 52.27, H 3.55, N 3.51.

(*R*)-1-(2-adamantan-1-yl-4,5-dihydro-oxazol-4-ylmethyl)-3-(2,4,6-trimethyl-phenyl)-3*H*-imidazol-1-ium **89h**



Synthesis according to the previous general procedure using tosylate **88f** (400 mg, 1.03 mmol), mesitylimidazole (191 mg, 1.03 mmol) and $NaBAr_F$ (913 mg, 1.03 mmol) yielded a colourless oil (835 mg, 64%, 0.660 mmol).

$[\alpha]_D^{20} = +14.3$ (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.59 (s, 1H; NC*H*N), 7.74 (mc, 8H; BAr_F *ortho* C*H*), 7.55 (mc, 4H; BAr_F para C*H*), 7.40 (mc, 1H; imid C*H*), 7.18 (mc, 1H; imid C*H*), 7.02 (mc, 2H; arom C*H*), 4.39 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.25 (mc, 1H; NCH_2), 3.98 (mc, 1H; NCH_2), 3.83 (mc, 1H; oxaz CH_2), 2.32 (s, 3H, $C_{arom}CH_3$), 2.01 (mc, 3H; adam C*H*), 1.99 (br, 3H, $C_{arom}CH_3$), 1.93 (br, 3H, $C_{arom}CH_3$), 1.83 (mc, 6H; adam CH_2), 1.75 (mc, 3H; adam CH_2), 1.66 (mc, 3H; adam CH_2);

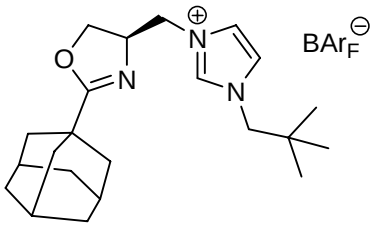
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 177.2 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 142.6 (arom *C*), 136.1 (N*C*HN), 134.7 (br, 8C; BAr_F *ortho C*H), 134.2 (arom *C*), 133.7 (arom *C*), 130.2 (arom *C*H), 129.8 (arom *C*H), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.9 (imid *C*H), 123.8 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 68.6 (oxaz *C*H_2), 64.8 (oxaz *C*H), 54.4 (N*C*H_2), 39.4 (adam *C*H_2), 36.2 (adam *C*H_2), 35.4 (adam *C*), 27.7 (adam *C*H), 20.9 ($C_{arom}CH_3$), 18.6 ($C_{arom}CH_3$), 16.8 ($C_{arom}CH_3$), 1 quat. C not detected;

IR (NaCl): $\tilde{\nu}$ = 2916w, 2854w, 1720w, 1634w, 1612w, 1551w, 1458w, 1350m, 1273s, 1111sbr, 972w, 933w, 887w, 841w, 748w, 710w, 671w cm^{-1};

MS (FAB): *m/z* (%): 404 (100) $[M - BAr_F]^+$;

EA calcd (%) for $C_{58}H_{46}BF_{24}N_3O$ (1267.78): C 54.95, H 3.66, N 3.31; found: C 54.65, H 3.93, N 3.44.

(*R*)-1-(2-adamantan-1-yl-4,5-dihydro-oxazol-4-ylmethyl)-3-(2,2-dimethyl-propyl)-3*H*-imidazol-1-ium **89i**



Synthesis according to the previous general procedure using tosylate **88f** (400 mg, 1.03 mmol), neopentylimidazole (142 mg, 1.03 mmol) and $NaBAr_F$ (913 mg, 1.03 mmol) yielded a white solid (829 mg, 66%, 0.680 mmol).

m.p. 85-86°C;

$[\alpha]_D^{20}$ = +29.7 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.50 (s, 1H; NC*H*N), 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.07 (mc, 1H; imid C*H*), 6.97 (mc, 1H; imid C*H*), 4.38 (mc, 1H; oxaz CH_2), 4.31 (mc, 1H; oxaz C*H*), 4.10 (mc, 1H; NCH_2), 3.90-3.75 (m, 4H; 1 x oxaz CH_2 + 1 x NCH_2 + 2 x CH_2C$(CH_3)_3$), 2.00 (mc, 3H; adam C*H*), 1.81 (mc, 6H; adam CH_2), 1.74 (mc, 3H; adam CH_2), 1.65 (mc, 3H; adam CH_2), 0.92 (mc, 9H; $CH_2C(CH_3)_3$);

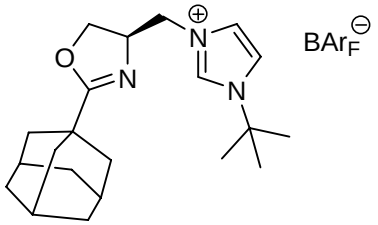
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 135.6 (N*C*HN), 134.7 (br, 8C; BAr_F *ortho C*H), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.4 (imid *C*H), 122.7 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 68.8 (oxaz *C*H_2), 64.4 (oxaz *C*H), 62.4 (*C*$H_2C(CH_3)_3$), 54.1 (N*C*H_2), 39.4 (adam *C*H_2), 36.2 (adam *C*H_2), 35.2 (adam *C*), 32.4 (CH_2*C*$(CH_3)_3$), 27.6 (adam *C*H), 26.5 (3C; CH_2C(*C*$H_3)_3$), 1 quat. C not detected;

IR (KBr): $\tilde{\nu}$ = 2908w, 2854w, 1643w, 1612w, 1558w, 1450w, 1350m, 1273s, 1111sbr, 987w, 933w, 887w, 833w, 741w, 710w, 671w cm^{-1};

MS (FAB): *m/z* (%): 356 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{54}H_{46}BF_{24}N_3O$ (1219.74): C 53.17, H 3.80, N 3.45; found: C 53.21, H 3.95, N 3.39.

(*R*)-1-(2-adamantan-1-yl-4,5-dihydro-oxazol-4-ylmethyl)-3-*tert*-butyl-3*H*-imidazol-1-ium **89j**



Synthesis according to the previous general procedure using tosylate **88f** (400 mg, 1.03 mmol), *tert*-butylimidazole (128 mg, 1.03 mmol) and $NaBAr_F$ (913 mg, 1.03 mmol) yielded a white solid (782 mg, 63%, 0.649 mmol).

m.p. 79-80°C;

$[\alpha]_D^{20}$ = +29.2 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.68 (s, 1H; NC*H*N), 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.17 (mc, 1H; imid C*H*), 7.07 (mc, 1H; imid C*H*), 4.37 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.11 (mc, 1H; NCH_2), 3.90-3.75 (m, 2H; oxaz CH_2 + NCH_2), 2.01 (mc, 3H; adam C*H*), 1.82 (mc, 6H; adam CH_2), 1.75 (mc, 3H; adam CH_2), 1.66 (mc, 3H; adam CH_2), 1.56 (mc, 9H; *t*Bu CH_3);

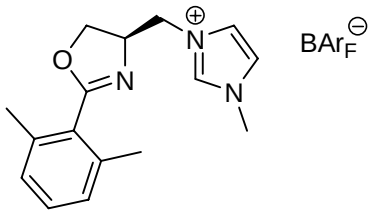
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.7 (br, 8C; BAr_F *ortho C*H), 133.0 (NCHN), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.4 (imid *C*H), 119.5 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 68.9 (oxaz *C*H_2), 64.1 (oxaz *C*H), 61.1 (*t*Bu *C*), 53.8 (N*C*H_2), 39.3 (adam *C*H_2), 36.2 (adam *C*H_2), 35.5 (adam *C*), 29.4 (3C; *t*Bu *C*H_3), 27.6 (adam *C*H), 1 quat. C not detected;

IR (KBr): $\tilde{\nu}$ = 2918w, 2856w, 1654w, 1610w, 1561w, 1456w, 1355m, 1277s, 1128sbr, 992w, 932w, 887w, 839w, 744w, 712w, 682w, 671w cm^{-1};

MS (FAB): *m/z* (%): 342 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{53}H_{44}BF_{24}N_3O$ (1205.71): C 52.80, H 3.68, N 3.49; found: C 52.92, H 3.91, N 3.43.

(*R*)-1-[2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazol-4-ylmethyl]-3-methyl-3*H*-imidazol-1-ium **89k**



Synthesis according to the previous general procedure using tosylate **88k** (400 mg, 1.11 mmol), methylimidazole (91 mg, 1.11 mmol) and $NaBAr_F$ (984 mg, 1.11 mmol) yielded a white solid (864 mg, 69%, 0.762 mmol).

m.p. 81-82°C;

$[\alpha]_D^{20}$ = +40.0 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.57 (s, 1H; NC*H*N), 7.71 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.25 (mc, 1H; arom C*H*), 7.08 (mc, 3H, 2 x arom C*H* + 1 x imid C*H*), 6.92 (mc, 1H, imid C*H*), 4.61 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.16 (mc, 1H; NCH_2), 4.03 (mc, 2H; oxaz CH_2 + NCH_2), 3.72 (s, 3H; NCH_3), 2.26 (s, 6H; $C_{arom}CH_3$);

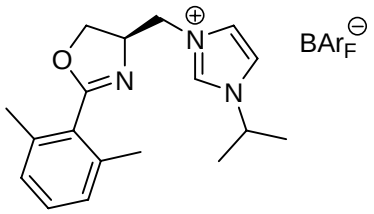
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 167.9 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 136.5 (2C; arom *C*CH_3), 135.5 (N*C*HN), 134.7 (br, 8C; BAr_F *ortho C*H), 130.4 (arom *C*H), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 127.8 (2C; arom *C*H), 127.1 (arom *C*), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.6 (imid *C*H), 123.1 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 68.8 (oxaz *C*H_2), 65.7 (oxaz *C*H), 54.4 (N*C*H_2), 36.5 (N*C*H_3), 19.5 (2C; $C_{arom}CH_3$);

IR (KBr): $\tilde{\nu}$ = 3165w, 3107w, 2927w, 1647w, 1610w, 1561w, 1467w, 1356m, 1286s, 1121sbr, 968w, 933w, 887w, 838w, 779w, 750w, 711w, 682w, 671w cm^{-1};

MS (FAB): *m/z* (%): 270 (100) $[M - BAr_F]^+$;

EA calcd (%) for $C_{48}H_{32}BF_{24}N_3O$ (1133.56): C 50.86, H 2.85, N 3.71; found: C 50.96, H 2.83, N 3.62.

(*R*)-1-[2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazol-4-ylmethyl]-3-isopropyl-3*H*-imidazol-1-ium **89l**



Synthesis according to the previous general procedure using tosylate **88k** (400 mg, 1.11 mmol), isopropylimidazole (122 mg, 1.11 mmol) and $NaBAr_F$ (984 mg, 1.11 mmol) yielded a white solid (788 mg, 61%, 0.678 mmol).

m.p. 113-114°C;

$[\alpha]_D^{20} = +35.1$ (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.62 (s, 1H; NC*H*N), 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.25 (mc, 1H; arom C*H*), 7.10-6.60 (m, 4H, 2 x arom C*H* + 2 x imid C*H*), 4.63 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.42 (sept, ^3J(H,H) = 6.7 Hz, 1H; C*H*$(CH_3)_2$), 4.18 (mc, 1H; NCH_2), 4.02 (mc, 2H; oxaz CH_2 + NCH_2), 2.26 (s, 6H; $C_{arom}CH_3$), 1.46 (mc, 6H; CH$(CH_3)_2$);

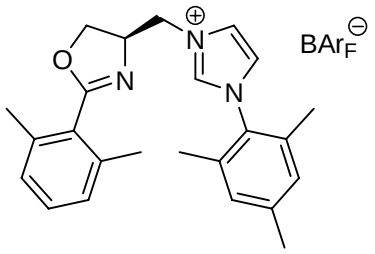
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 167.9 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 136.7 (2C; arom *C*CH_3), 134.7 (br, 8C; BAr_F *ortho C*H), 133.4 (N*C*HN), 130.4 (arom *C*H), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 127.8 (2C; arom *C*H), 127.0 (arom *C*), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.6 (imid *C*H), 119.9 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 68.8 (oxaz *C*H_2), 65.6 (oxaz *C*H), 54.4 (*C*H$(CH_3)_2$), 54.2 (NCH_2), 22.5 (CH(*C*$H_3)_2$), 22.5 (CH(*C*$H_3)_2$), 19.7 (2C; $C_{arom}CH_3$);

IR (KBr): $\tilde{\nu}$ = 3155w, 2986w, 1659w, 1612w, 1558w, 1465w, 1351m, 1273s, 1111sbr, 964w, 933w, 887w, 841w, 779w, 740w, 710w, 671w cm^{-1};

MS (FAB): *m/z* (%): 298 (100) $[M - BAr_F]^+$;

EA calcd (%) for $C_{50}H_{36}BF_{24}N_3O$ (1161.61): C 51.70, H 3.12, N 3.62; found: C 51.72, H 3.05, N 3.54.

(*R*)-1-[2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazol-4-ylmethyl]-3-(2,4,6-trimethyl-phenyl)-3*H*-imidazol-1-ium **89m**



Synthesis according to the previous general procedure using tosylate **88k** (400 mg, 1.11 mmol), mesitylimidazole (207 mg, 1.11 mmol) and $NaBAr_F$ (984 mg, 1.11 mmol) yielded a white solid (896 mg, 65%, 0.723 mmol).

m.p. 78-79°C;

$[\alpha]_D^{20}$ = +22.9 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.68 (s, 1H; NC*H*N), 7.72 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.36 (mc, 1H; imid C*H*), 7.24 (mc, 1H; $arom_{oxaz}$ C*H*), 7.17 (mc, 1H; imid C*H*), 7.07 (mc, 2H, $arom_{imid}$ C*H*), 7.01 (mc, 2H, $arom_{oxaz}$ C*H*), 4.65 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.33 (mc, 1H; NCH_2), 4.17 (mc, 1H; oxaz CH_2), 4.06 (mc, 1H; NCH_2), 3.72 (s, 3H; NCH_3), 2.32 (mc, 6H; $C_{arom\ oxaz}CH_3$), 2.27 (s, 3H, $C_{arom\ imid}CH_3$), 1.91 (br, 6H, $C_{arom\ imid}CH_3$);

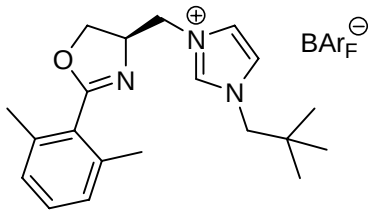
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 167.8 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 142.6 ($arom_{imid}$ *C*), 136.7 (2C; $arom_{oxaz}$ *C*CH_3), 136.3 (N*C*HN), 134.7 (br, 8C; BAr_F *ortho C*H), 134.0 ($arom_{imid}$ *C*), 133.8 ($arom_{imid}$ *C*), 130.4 ($arom_{oxaz}$ *C*H), 130.2 ($arom_{imid}$ *C*H), 130.1 ($arom_{imid}$ *C*H), 129.8 ($arom_{imid}$ *C*), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 127.8 (2C; $arom_{oxaz}$ *C*H), 127.0 ($arom_{oxaz}$ *C*), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 124.0 (imid *C*H), 123.4 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 68.7 (oxaz *C*H_2), 65.9 (oxaz *C*H), 54.6 (N*C*H_2), 20.9 ($C_{arom\ imid}CH_3$), 19.7 (2C; $C_{arom\ oxaz}CH_3$), 16.8 ($C_{arom\ imid}CH_3$), 16.8 ($C_{arom\ imid}CH_3$);

IR (KBr): $\tilde{\nu}$ = 3165w, 3012w, 2927w, 1647w, 1610w, 1575w, 1561w, 1467w, 1357m, 1286s, 1116sbr, 968w, 933w, 886w, 838w, 780w, 750w, 711w, 682w, 671w, 622w cm^{-1};

MS (FAB): *m/z* (%): 374 (100) [M - BAr_F]$^+$, 187 (93);

EA calcd (%) for $C_{56}H_{40}BF_{24}N_3O$ (1237.71): C 54.34, H 3.26, N 3.39; found: C 54.25, H 3.24, N 3.08.

(*R*)-1-[2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazol-4-ylmethyl]-3-(2,2-dimethyl-propyl)-3*H*-imidazol-1-ium **89n**



Synthesis according to the previous general procedure using tosylate **88k** (400 mg, 1.11 mmol), neopentylimidazole (153 mg, 1.11 mmol) and $NaBAr_F$ (984 mg, 1.11 mmol) yielded a white solid (863 mg, 65%, 0.725 mmol).

m.p. 141-142°C;

$[\alpha]_D^{20}$ = +35.7 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.56 (s, 1H; NC*H*N), 7.72 (mc, 8H; BAr_F *ortho* C*H*), 7.55 (mc, 4H; BAr_F para C*H*), 7.25 (mc, 1H; arom C*H*), 7.20-6.80 (m, 4H, 2 x arom C*H* + 2 x imid C*H*), 4.62 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.25 (mc, 1H; NCH_2), 4.06 (mc, 2H; oxaz CH_2 + NCH_2), 3.80 (mc, 2H; NCH_2C$(CH_3)_3$), 2.27 (s, 6H; $C_{arom}CH_3$), 0.88 (mc, 9H; $NCH_2C(CH_3)_3$);

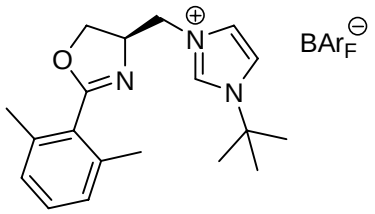
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 167.8 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 136.7 (2C; arom *C*CH_3), 135.6 (N*C*HN), 134.7 (br, 8C; BAr_F *ortho C*H), 130.4 (arom *C*H), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 127.8 (2C; arom *C*H), 127.0 (arom *C*), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.5 (imid *C*H), 123.4 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 68.7 (oxaz *C*H_2), 65.8 (oxaz *C*H), 62.4 (N*C*H_2C$(CH_3)_3$), 54.3 (N*C*H_2), 32.4 (NCH_2*C*$(CH_3)_3$), 26.5 (3C; NCH_2C(*C*$H_3)_3$), 19.7 (2C; C_{arom}*C*H_3);

IR (KBr): $\tilde{\nu}$ = 3163w, 2970w, 1659w, 1612w, 1558w, 1473w, 1350m, 1273s, 1111sbr, 964w, 888w, 841w, 779w, 748w, 710w, 671w cm^{-1};

MS (FAB): *m/z* (%): 326 (100) $[M - BAr_F]^+$;

EA calcd (%) for $C_{52}H_{40}BF_{24}N_3O$ (1189.67): C 52.50, H 3.39, N 3.53; found: C 52.06, H 3.36, N 3.38.

(*R*)-3-*tert*-butyl-1-[2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazol-4-ylmethyl]-3*H*-imidazol-1-ium **89o**



Synthesis according to the previous general procedure using tosylate **88k** (400 mg, 1.11 mmol), *tert*-butylimidazole (138 mg, 1.11 mmol) and $NaBAr_F$ (984 mg, 1.11 mmol) yielded a white solid (709 mg, 54%, 0.603 mmol).

m.p. 135-136°C;

$[\alpha]_D^{20}$ = +39.9 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.61 (s, 1H; NC*H*N), 7.71 (mc, 8H; BAr_F *ortho* C*H*), 7.54 (mc, 4H; BAr_F para C*H*), 7.25 (mc, 1H; arom C*H*), 7.19 (mc, 1H, imid C*H*), 7.16 (mc, 1H, imid C*H*), 7.08 (mc, 2H; arom C*H*), 4.62 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.21 (mc, 1H; NCH_2), 4.03 (mc, 2H; oxaz CH_2 + NCH_2), 2.26 (s, 6H; $C_{arom}CH_3$), 1.53 (mc, 9H; *t*Bu CH_3);

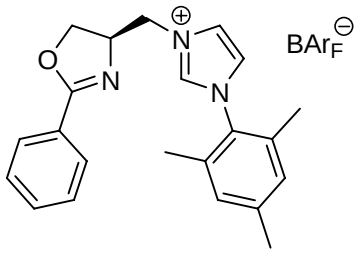
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 167.7 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 136.7 (2C; arom *C*CH_3), 134.7 (br, 8C; BAr_F *ortho C*H), 132.7 (N*C*HN), 130.3 (arom *C*H), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 127.9 (2C; arom *C*H), 127.0 (arom *C*), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.6 (imid *C*H), 119.7 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 68.7 (oxaz *C*H_2), 65.7 (oxaz *C*H), 61.4 (*t*Bu *C*), 54.2 (N*C*H_2), 29.4 (*t*Bu *C*H_3), 19.7 (2C; $C_{arom}CH_3$);

IR (KBr): $\tilde{\nu}$ = 3173w, 2993w, 1670w, 1610w, 1552w, 1468w, 1354m, 1273s, 1121sbr, 962w, 935w, 888w, 839w, 786w, 744w, 713w, 682w, 671w, 626w cm^{-1};

MS (FAB): *m/z* (%): 312 (100) $[M - BAr_F]^+$;

EA calcd (%) for $C_{51}H_{38}BF_{24}N_3O$ (1175.64): C 52.10, H 3.26, N 3.57; found: C 51.92, H 3.27, N 3.51.

(*R*)-1-(2-phenyl-4,5-dihydro-oxazol-4-ylmethyl)-3-(2,4,6-trimethyl-phenyl)-3*H*-imidazol-1-ium **89p**



Synthesis according to the previous general procedure using tosylate **88p** (250 mg, 0.749 mmol), mesitylimidazole (83 mg, 0.749 mmol) and $NaBAr_F$ (664 mg, 0.749 mmol) yielded a colourless oil (601 mg, 69%, 0.517 mmol).

$[\alpha]_D^{20}$ = +29.5 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 8.50 (s, 1H; NC*H*N), 7.85 (d, ^3J(H,H) = 7.8 Hz, 2H; arom$_{oxaz}$ C*H*), 7.72 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 5H; 4 x BAr_F para C*H* + 1 x arom$_{oxaz}$ C*H*), 7.40 (t, ^3J(H,H) = 7.8 Hz, 2H; arom$_{oxaz}$ C*H*), 7.37 (mc, 1H; imid C*H*), 7.16 (mc, 1H; imid C*H*), 7.03 (br, 1H; arom$_{imid}$ C*H*), 6.98 (br, 1H; arom$_{imid}$ C*H*), 4.67 (mc, 1H; oxaz C*H*), 4.61 (mc, 1H; oxaz CH_2), 4.44 (mc, 1H; NCH_2), 4.16 (mc, 1H; NCH_2), 4.08 (mc, 1H; oxaz CH_2), 2.32 (s, 3H, $C_{arom}CH_3$), 1.98 (br, 3H, $C_{arom}CH_3$), 1.77 (br, 3H, $C_{arom}CH_3$);

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 167.2 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 142.8 (arom$_{imid}$ *C*), 136.1 (N*C*HN), 134.9 (br, 8C; BAr_F *ortho* *C*H), 133.9 (arom$_{imid}$ *C*), 133.8 (arom$_{imid}$ *C*), 132.9 (arom$_{oxaz}$ *C*H), 130.3 (2C; arom$_{imid}$ *C*H), 129.8 (arom$_{imid}$ *C*), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 128.9 (2C; arom$_{oxaz}$ *C*H), 128.5 (2C; arom$_{oxaz}$ *C*H), 125.9 (arom$_{oxaz}$ *C*), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 124.2 (imid *C*H), 123.7 (imid *C*H), 117.7 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 69.1 (oxaz *C*H_2), 65.3 (oxaz *C*H), 54.1 (N*C*H_2), 21.1 ($C_{arom}CH_3$), 17.0 ($C_{arom}CH_3$), 16.7 ($C_{arom}CH_3$);

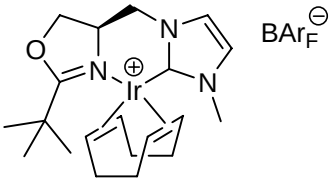
IR (NaCl): $\tilde{\nu}$ = 3159w, 2963w, 2927w,1704w, 1645w, 1610w, 1550w, 1452w, 1354m, 1273s, 1121sbr, 977w, 932w, 888w, 839w, 782w, 743w, 698w, 671w cm^{-1};

MS (FAB): *m/z* (%): 346 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{54}H_{36}BF_{24}N_3O$ (1209.66): C 53.62, H 2.91, N 3.47; found: C 53.54, H 3.10, N 3.33.

6.3.11 Synthesis of iridium complexes 90a-p

(*R*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(2-*tert*-butyl-4,5-dihydro-oxazol-4-ylmethyl)-3-methyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90a**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89a** (200 mg, 0.184 mmol), [(η^4-cod)IrCl]$_2$ (62 mg, 0.092 mmol) and NaO*t*Bu (18 mg, 0.184 mmol) yielded an orange solid (209 mg, 82%, 0.151 mmol).

$[\alpha]_D^{20}$ = +72 (c = 0.150, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.68 (mc, 1H; imid C*H*), 6.65 (mc, 1H; imid C*H*), 5.21 (mc, 1H; NCH_2), 4.61 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.52 (mc, 1H; cod C*H*), 4.37 (mc, 1H; cod C*H*), 4.01 (mc, 1H; cod C*H*), 3.81 (mc, 3H; cod C*H* + NCH_2 + oxaz CH_2), 3.66 (s, 3H, NCH_3), 2.33 (mc, 1H; cod CH_2), 2.24 (mc, 1H; cod CH_2), 2.10 (mc, 2H; cod CH_2), 1.91 (mc, 2H; cod CH_2), 1.75 (mc, 2H; cod CH_2), 1.22 (s, 9H; *t*Bu CH_3);

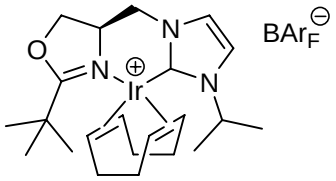
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 181.2 (O*C*N), 175.4 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.8 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 122.4 (imid *C*H), 122.1 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 86.0 (cod *C*H), 80.3 (cod *C*H), 71.0 (oxaz *C*H_2), 62.5 (cod *C*H), 62.4 (oxaz *C*H), 57.8 (cod *C*H), 51.6 (N*C*H_2), 37.1 (N*C*H_3), 33.9 (*t*Bu *C*), 32.9 (cod *C*H_2), 32.4 (cod *C*H_2), 29.8 (cod *C*H_2), 29.0 (cod *C*H_2), 28.5 (3C; *t*Bu *C*H_3);

IR (KBr): $\tilde{\nu}$ = 2968w, 2892w, 1610m, 1459w, 1406w, 1356m, 1279s, 1134bs, 889w, 839w, 716w, 685w, 669w cm^{-1};

MS (FAB): *m/z* (%): 522 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{52}H_{43}BF_{24}IrN_3O$ (1384.91): C 45.10, H 3.13, N 3.03; found: C 45.05, H 3.18, N 3.10.

(*R*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(2-*tert*-butyl-4,5-dihydro-oxazol-4-ylmethyl)-3-isopropyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90b**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89b** (200 mg, 0.180 mmol), [(η^4-cod)IrCl]$_2$ (60 mg, 0.090 mmol) and NaO*t*Bu (17 mg, 0.148 mmol) yielded an orange solid (178 mg, 70%, 0.126 mmol).

$[\alpha]_D^{20}$ = +79 (c = 0.191, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.80 (mc, 1H; imid C*H*), 6.73 (mc, 1H; imid C*H*), 5.25 (mc, 1H; NCH_2), 4.61 (mc, 3H; oxaz CH_2 + oxaz C*H* + *i*Pr C*H*), 4.45 (mc, 1H; cod C*H*), 4.35 (mc, 1H; cod C*H*), 3.85 (mc, 2H; cod C*H*), 3.80 (mc, 2H; NCH_2 + oxaz CH_2), 2.28 (mc, 2H; cod CH_2), 2.10 (mc, 2H; cod CH_2), 2.01 (mc, 1H; cod CH_2), 1.85 (mc, 1H; cod CH_2), 1.78 (mc, 1H; cod CH_2), 1.65 (mc, 1H; cod CH_2), 1.36 (d, ^3J(H,H) = 7.1 Hz, 3H; *i*Pr CH_3), 1.29 (d, ^3J(H,H) = 7.1 Hz, 3H; *i*Pr CH_3), 1.24 (s, 9H; *t*Bu CH_3);

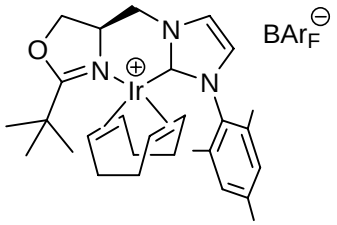
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 181.1 (O*C*N), 174.0 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.8 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.1 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 116.6 (imid *C*H), 85.3 (cod *C*H), 79.7 (cod *C*H), 70.9 (oxaz *C*H_2), 62.9 (cod *C*H), 62.5 (oxaz *C*H), 57.8 (cod *C*H), 52.3 (*i*Pr *C*H), 51.3 (N*C*H_2), 33.8 (*t*Bu *C*), 33.3 (cod *C*H_2), 32.1 (cod *C*H_2), 29.6 (cod *C*H_2), 29.1 (cod *C*H_2), 28.5 (3C; *t*Bu *C*H_3), 24.9 (*i*Pr *C*H_3), 22.2 (*i*Pr *C*H_3);

IR (KBr): $\tilde{\nu}$ = 2982w, 1611m, 1425w, 1356m, 1275s, 1126bs, 886w, 839w, 714w, 681w, 670w cm^{-1};

MS (FAB): *m/z* (%): 550 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{54}H_{47}BF_{24}IrN_3O$ (1412.96): C 45.90, H 3.35, N 2.97; found: C 45.93, H 3.30, N 3.00.

(*R*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(2-*tert*-butyl-4,5-dihydro-oxazol-4-ylmethyl)-3-(2,4,6-trimethyl-phenyl)-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90c**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89c** (222 mg, 0.186 mmol), [(η^4-cod)IrCl]$_2$ (63 mg, 0.093 mmol) and NaO*t*Bu (18 mg, 0.186 mmol) yielded an orange solid (149 mg, 54%, 0.100 mmol).

$[\alpha]_D^{20}$ = +58 (c = 0.164, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.71 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.99 (mc, 1H, arom C*H*), 6.95 (mc, 1H, arom C*H*), 6.84 (mc, 1H; imid C*H*), 6.73 (mc, 1H; imid C*H*), 4.88 (mc, 1H; oxaz C*H*), 4.81 (mc, 1H; NCH_2), 4.51 (mc, 1H; oxaz CH_2), 4.34 (mc, 1H; cod C*H*), 3.97 (mc, 1H; oxaz CH_2), 3.88 (mc, 2H; cod C*H* + NCH_2), 3.61 (mc, 1H; cod C*H*), 3.10 (mc, 1H; cod C*H*), 2.32 (s, 3H; $C_{arom}CH_3$), 2.07 (mc, 1H; cod CH_2), 1.97 (mc, 8H; 3 x $C_{arom}CH_3$ + 2 x cod CH_2), 1.85 (mc, 1H; cod CH_2), 1.74 (mc, 1H; cod CH_2), 1.68 (mc, 1H; cod CH_2), 1.52 (mc, 1H; cod CH_2), 1.36 (s, 9H; *t*Bu CH_3);

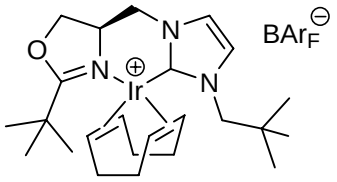
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 180.8 (O*C*N), 171.8 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 140.3 (arom *C*), 134.8 (br, 8C; BAr_F *ortho* *C*H), 134.6 (arom *C*), 134.3 (arom *C*), 134.1 (arom *C*), 129.6 (arom *C*H), 129.3 (arom *C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 124.1 (imid *C*H), 122.4 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 85.1 (cod *C*H), 76.6 (cod *C*H), 70.2 (oxaz *C*H_2), 64.0 (cod *C*H), 62.3 (oxaz *C*H), 62.0 (cod *C*H), 50.7 (N*C*H_2), 34.1 (2C; cod *C*H_2 overlap with *t*Bu *C*), 31.3 (cod *C*H_2), 31.0 (cod *C*H_2), 28.7 (3C; *t*Bu *C*H_3), 27.7 (cod *C*H_2), 21.0 ($C_{arom}CH_3$), 18.6 ($C_{arom}CH_3$), 17.5 ($C_{arom}CH_3$);

IR (KBr): $\tilde{\nu}$ = 2960w, 1611m, 1482w, 1356m, 1275s, 1127bs, 887w, 839w, 713w, 682w, 670w cm^{-1};

MS (FAB): *m/z* (%): 626 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{60}H_{51}BF_{24}IrN_3O$ (1489.06): C 48.40, H 3.45, N 2.82; found: C 48.66, H 3.35, N 2.98.

(*R*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(2-*tert*-butyl-4,5-dihydro-oxazol-4-ylmethyl)-3-(2,2-dimethyl-propyl)-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90d**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89d** (200 mg, 0.175 mmol), [(η^4-cod)IrCl]$_2$ (59 mg, 0.087 mmol) and NaO*t*Bu (17 mg, 0.175 mmol) yielded an orange solid (161 mg, 64%, 0.112 mmol).

$[\alpha]_D^{20}$ = +83 (c = 0.153, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.89 (mc, 1H; imid C*H*), 6.77 (mc, 1H; imid C*H*), 5.35 (mc, 1H; NCH_2), 4.60 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.45 (mc, 1H; cod C*H*), 4.22 (mc, 1H; cod C*H*), 3.95 (mc, 3H; 2 x cod C*H* + 1 x NCH_2C$(CH_3)_3$), 3.80 (mc, 2H; NCH_2 + oxaz CH_2), 3.55 (mc, 1H; NCH_2C$(CH_3)_3$), 2.27 (mc, 2H; cod CH_2), 2.16 (mc, 1H; cod CH_2), 2.05 (mc, 2H; cod CH_2), 1.93 (mc, 1H; cod CH_2), 1.71 (mc, 1H; cod CH_2), 1.60 (mc, 1H; cod CH_2), 1.20 (s, 9H; *t*Bu CH_3), 0.93 (s, 9H, NCH$_2$C(C$H_3)_3$);

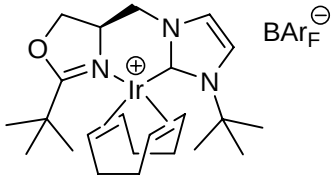
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 181.2 (O*C*N), 176.3 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.8 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F$_3$), 122.8 (imid *C*H), 121.5 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 85.3 (cod *C*H), 78.6 (cod *C*H), 70.8 (oxaz *C*H$_2$), 62.8 (cod *C*H), 62.5 (oxaz *C*H), 61.1 (N*C*H$_2$C$(CH_3)_3$), 60.0 (cod *C*H), 51.9 (N*C*H$_2$), 33.9 (*t*Bu *C*), 33.7 (cod *C*H$_2$), 32.0 (NCH$_2$*C*$(CH_3)_3$), 31.7 (cod *C*H$_2$), 29.8 (cod *C*H$_2$), 28.9 (cod *C*H$_2$), 28.4 (3C; *t*Bu *C*H$_3$), 27.7 (NCH$_2$C(*C*H$_3)_3$);

IR (KBr): $\tilde{\nu}$ = 2982w, 1612w, 1439w, 1356m, 1278s, 1126bs, 888w, 839w, 713w, 681w, 671w cm^{-1};

MS (FAB): *m/z* (%): 578 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{56}H_{51}BF_{24}IrN_3O$ (1441.01): C 46.68, H 3.57, N 2.92; found: C 46.73, H 3.43, N 2.98.

(*R*)-{(η^4-1,5-cyclooctadiene)-[1-(2-*tert*-butyl-4,5-dihydro-oxazol-4-ylmethyl)-3-*tert*-butyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90e**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89e** (200 mg, 0.177 mmol), [(η^4-cod)IrCl]$_2$ (60 mg, 0.088 mmol) and NaO*t*Bu (17 mg, 0.177 mmol) yielded an orange/yellow solid (174 mg, 69%, 0.122 mmol).

$[\alpha]_D^{20}$ = +55 (c = 0.113, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.96 (mc, 1H; imid C*H*), 6.70 (mc, 1H; imid C*H*), 5.55 (mc, 1H; NCH_2), 4.61 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.25 (mc, 2H; cod C*H*), 4.02 (mc, 1H; cod C*H*), 3.88 (mc, 2H; cod C*H* + NCH_2), 3.70 (mc, 2H; oxaz CH_2), 2.38 (mc, 1H; cod CH_2), 2.15 (mc, 3H; cod CH_2), 2.03 (mc, 1H; cod CH_2), 1.88 (mc, 1H; cod CH_2), 1.64 (mc, 10H; 1 x cod CH_2 + 9 x *t*Bu$_{imid}$ CH_3), 1.51 (mc, 1H; cod CH_2), 1.21 (s, 9H; *t*Bu$_{oxaz}$ CH_3);

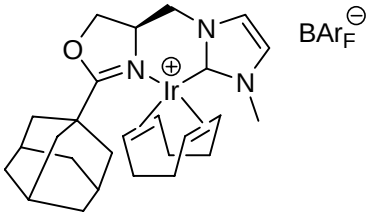
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 181.3 (O*C*N), 174.2 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.8 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 122.0 (imid *C*H), 119.0 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 82.6 (cod *C*H), 77.8 (cod *C*H), 70.2 (oxaz *C*H_2), 63.8 (cod *C*H), 63.2 (oxaz *C*H), 58.9 (*t*Bu$_{imid}$ *C*), 58.5 (cod *C*H), 51.5 (N*C*H_2), 34.0 (*t*Bu$_{oxaz}$ *C*), 34.0 (cod *C*H_2), 32.3 (3C; *t*Bu$_{imid}$ *C*H_3), 30.7 (cod *C*H_2), 30.5 (cod *C*H_2), 28.3 (3C; *t*Bu$_{oxaz}$ *C*H_3), 28.0 (cod *C*H_2);

IR (KBr): $\tilde{\nu}$ = 2974w, 1611w, 1481w, 1424w, 1404w, 1356m, 1275s, 1134bs, 888w, 839w, 713w, 682w, 671w cm^{-1};

MS (FAB): *m/z* (%): 564 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{55}H_{49}BF_{24}IrN_3O$ (1426.97): C 46.29, H 3.46, N 2.94; found: C 45.98, H 3.44, N 2.80.

(*R*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(2-adamantan-1-yl-4,5-dihydro-oxazol-4-ylmethyl)-3-methyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90f**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89f** (250 mg, 0.215 mmol), [(η^4-cod)IrCl]$_2$ (72 mg, 0.107 mmol) and NaO*t*Bu (21 mg, 0.215 mmol) yielded an orange solid (208 mg, 66%, 0.142 mmol).

$[\alpha]_D^{20}$ = +61 (c = 0.174, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.71 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.65 (mc, 2H; imid C*H*), 5.18 (mc, 1H; NCH_2), 4.58 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.54 (mc, 1H; cod C*H*), 4.47 (mc, 1H; cod C*H*), 3.97 (mc, 1H; cod C*H*), 3.78 (mc, 2H; NCH_2 + oxaz CH_2), 3.67 (s, 3H, NCH_3), 2.32 (mc, 2H; cod CH_2), 2.25 (mc, 5H; 2 x cod CH_2 + 3 x adam C*H*), 1.93 (mc, 2H; cod CH_2), 1.90-1.70 (m, 11H; 2 x cod CH_2 + 9 x adam CH_2), 1.67 (mc, 3H; adam CH_2);

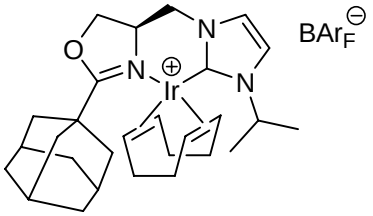
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 180.7 (O*C*N), 175.4 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.8 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 122.4 (imid *C*H), 122.1 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 85.9 (cod *C*H), 79.8 (cod *C*H), 70.6 (oxaz *C*H_2), 62.2 (cod *C*H), 61.9 (oxaz *C*H), 57.0 (cod *C*H), 51.7 (N*C*H_2), 40.1 (3C; adam *C*H_2), 37.2 (N*C*H_3) 36.0 (adam *C*), 35.9 (3C; adam *C*H_2), 32.9 (cod *C*H_2), 32.5 (cod *C*H_2), 29.8 (cod *C*H_2), 29.1 (cod *C*H_2), 27.5 (3C; adam *C*H);

IR (KBr): $\tilde{\nu}$ = 2918w, 2857w, 1607m, 1457w, 1356m, 1278s, 1125bs, 887w, 838w, 714w, 685w, 670w cm^{-1};

MS (FAB): *m/z* (%): 600 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{58}H_{49}BF_{24}IrN_3O$ (1463.02): C 47.62, H 3.38, N 2.87; found: C 47.27, H 3.41, N 2.69.

(*R*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(2-adamantan-1-yl-4,5-dihydro-oxazol-4-ylmethyl)-3-isopropyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90g**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89g** (200 mg, 0.168 mmol), [(η^4-cod)IrCl]$_2$ (56 mg, 0.084 mmol) and NaO*t*Bu (16 mg, 0.168 mmol) yielded an orange solid (130 mg, 52%, 0.087 mmol).

$[\alpha]_D^{20}$ = +65 (c = 0.141, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.71(mc, 8H; BAr_F *ortho* C*H*), 7.54 (mc, 4H; BAr_F para C*H*), 6.80 (mc, 1H; imid C*H*), 6.72 (mc, 1H; imid C*H*), 5.22 (mc, 1H; NCH_2), 4.55 (mc, 3H; oxaz CH_2 + oxaz C*H* + *i*Pr C*H*), 4.46 (mc, 1H; cod C*H*), 4.41 (mc, 1H; cod C*H*), 3.88 (mc, 1H; cod C*H*), 3.83 (mc, 1H; cod C*H*), 3.77 (mc, 2H; NCH_2 + oxaz CH_2), 2.27 (mc, 2H; cod CH_2), 2.10 (mc, 2H; cod CH_2), 2.06 (mc, 4H; 1 x cod CH_2 + 3 x adam C*H*), 1.87 (mc, 7H; 1 x cod CH_2 + 6 x adam CH_2), 1.79 (mc, 4H; 1 x cod CH_2 + 3 x adam CH_2), 1.66 (mc, 4H; 1 x cod CH_2 + 3 x adam CH_2), 1.38 (d, ^3J(H,H) = 7.2 Hz, 3H; *i*Pr CH_3), 1.29 (d, ^3J(H,H) = 6.9 Hz, 3H; *i*Pr CH_3);

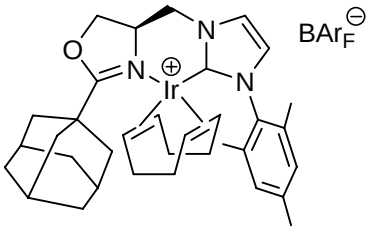
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 180.6 (O*C*N), 174.1 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.8 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.1 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 116.5 (imid *C*H), 85.4 (cod *C*H), 79.2 (cod *C*H), 70.6 (oxaz *C*H_2), 62.5 (cod *C*H), 62.0 (oxaz *C*H), 57.3 (cod *C*H), 52.4 (*i*Pr *C*H), 51.6 (N*C*H_2), 40.0 (3C; adam *C*H_2), 36.0 (adam *C*), 35.9 (3C; adam *C*H_2), 33.4 (cod *C*H_2), 32.0 (cod *C*H_2), 29.9 (cod *C*H_2), 29.1 (cod *C*H_2), 27.5 (3C; adam *C*H), 25.2 (*i*Pr *C*H_3), 22.2 (*i*Pr *C*H_3);

IR (KBr): $\tilde{\nu}$ = 2916w, 1608m, 1425w, 1355m, 1278s, 1126bs, 888w, 839w, 713w, 682w, 671w cm^{-1};

MS (FAB): *m/z* (%): 628 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{60}H_{53}BF_{24}IrN_3O$ (1491.07): C 48.33, H 3.58, N 2.82; found: C 48.06, H 3.55, N 2.68.

(*R*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(2-adamantan-1-yl-4,5-dihydro-oxazol-4-ylmethyl)-3-(2,4,6-trimethyl-phenyl)-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90h**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89h** (240 mg, 0.189 mmol), [(η^4-cod)IrCl]$_2$ (64 mg, 0.095 mmol) and NaO*t*Bu (18 mg, 0.189 mmol) yielded an orange solid (187 mg, 63%, 0.119 mmol).

$[\alpha]_D^{20}$ = +48 (c = 0.177, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.71 (mc, 8H; BAr_F *ortho* C*H*), 7.52 (mc, 4H; BAr_F para C*H*), 7.00 (mc, 1H, arom C*H*), 6.95 (mc, 1H, arom C*H*), 6.80 (mc, 1H; imid C*H*), 6.72 (mc, 1H; imid C*H*), 4.95 (mc, 1H; oxaz C*H*), 4.67 (mc, 1H; NCH_2), 4.43 (mc, 1H; oxaz CH_2), 4.29 (mc, 1H; cod C*H*), 3.98 (mc, 2H; oxaz CH_2 + cod C*H*), 3.88 (mc, 1H; NCH_2), 3.59 (mc, 1H; cod C*H*), 3.07 (mc, 1H; cod C*H*), 2.34 (s, 3H; $C_{arom}CH_3$), 2.20-2.00 (m, 11H; 3 x adam CH_2 + 3 x adam C*H* + 3 x $C_{arom}CH_3$ + 2 x cod CH_2), 2.00-1.82 (m, 8H; 3 x adam CH_2 + 3 x $C_{arom}CH_3$ + 2 x cod CH_2), 1.82-1.75 (m, 3H; 3 x adam CH_2), 1.75-1.60 (m, 6H; 3 x adam CH_2 +3 x cod CH_2), 1.60-1.50 (m, 1H; cod CH_2);

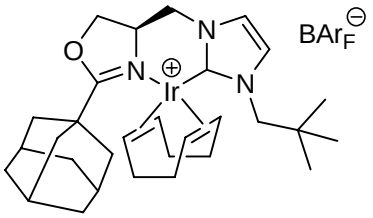
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 180.1 (O*C*N), 170.9 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 140.3 (arom *C*), 134.8 (br, 8C; BAr_F *ortho* *C*H), 134.5 (arom *C*), 134.3 (arom *C*), 134.2 (arom *C*), 129.7 (arom *C*H), 129.3 (arom *C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 124.3 (imid *C*H), 122.3 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 84.5 (cod *C*H), 76.0 (cod *C*H), 69.7 (oxaz *C*H_2), 63.6 (cod *C*H), 61.9 (oxaz *C*H), 61.9 (cod *C*H), 51.0 (N*C*H_2), 39.6 (3C; adam *C*H_2), 36.3 (adam *C*), 35.9 (3C; adam *C*H_2), 34.0 (cod *C*H_2), 31.4 (cod *C*H_2), 30.8 (cod *C*H_2), 28.0 (cod *C*H_2), 27.5 (3C; adam *C*H), 21.0 ($C_{arom}CH_3$), 18.8 ($C_{arom}CH_3$), 17.6 ($C_{arom}CH_3$);

IR (KBr): $\tilde{\nu}$ = 2920w, 1609m, 1456w, 1356m, 1278s, 1126bs, 887w, 713w, 684w cm^{-1};

MS (FAB): *m/z* (%): 704 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{66}H_{57}BF_{24}IrN_3O$ (1567.17): C 50.58, H 3.67, N 2.68; found: C 50.57, H 3.68, N 2.75.

(*R*)-{(η^4-1,5-cyclooctadiene)-[1-(2-adamantan-1-yl-4,5-dihydro-oxazol-4-ylmethyl)-3-(2,2-dimethyl-propyl)-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90i**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89i** (213 mg, 0.175 mmol), [(η^4-cod)IrCl]$_2$ (59 mg, 0.087 mmol) and NaO*t*Bu (17 mg, 0.175 mmol) yielded an orange solid (133 mg, 50%, 0.087 mmol).

$[\alpha]_D^{20}$ = +33 (c = 0.129, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.71 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.89 (mc, 1H; imid C*H*), 6.75 (mc, 1H; imid C*H*), 5.34 (mc, 1H; NCH_2), 4.55 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.44 (mc, 1H; cod C*H*), 4.31 (mc, 1H; cod C*H*), 3.95 (mc, 3H; 2 x cod C*H* + 1 x NCH_2C(CH$_3$)$_3$), 3.81 (mc, 2H; NCH_2 + oxaz CH_2), 3.52 (mc, 1H; NCH_2C(CH$_3$)$_3$), 2.27 (mc, 2H; cod CH_2), 2.17 (mc, 1H; cod CH_2), 2.05 (mc, 5H; 3 x adam C*H* + 2 x cod CH_2), 1.94 (mc, 1H; cod CH_2), 1.85 (mc, 3H; adam CH_2), 1.78 (mc, 6H; adam CH_2), 1.71 (mc, 1H; cod CH_2), 1.63 (mc, 4H; 1 x cod CH_2 + 3 x adam CH_2), 0.95 (s, 9H, NCH$_2$C(C*H*$_3$)$_3$);

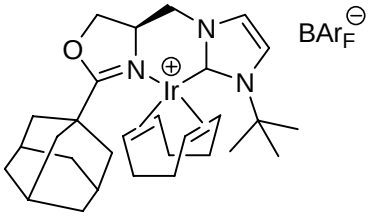
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 181.2 (O*C*N), 176.4 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.8 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F$_3$), 122.9 (imid *C*H), 121.4 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 85.2 (cod *C*H), 78.4 (cod *C*H), 70.5 (oxaz *C*H$_2$), 62.5 (cod *C*H), 62.0 (oxaz *C*H), 61.3 (NCH_2C(CH$_3$)$_3$), 59.2 (cod *C*H), 52.1 (N*C*H$_2$), 39.9 (3C; adam *C*H$_2$), 36.3 (adam *C*), 35.9 (3C; adam *C*H$_2$), 33.8 (cod *C*H$_2$), 32.0 (NCH$_2$*C*(CH$_3$)$_3$), 31.7 (cod *C*H$_2$), 30.0 (cod *C*H$_2$), 29.0 (cod *C*H$_2$), 27.7 (3C; *t*Bu *C*H$_3$), 27.5 (NCH$_2$C(*C*H$_3$)$_3$);

IR (KBr): $\tilde{\nu}$ = 2917w, 1607w, 1455w, 1423w, 1400w, 1355m, 1278s, 1126bs, 887w, 839w, 713w, 681w, 670w cm^{-1};

MS (FAB): *m/z* (%): 656 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{62}H_{57}BF_{24}IrN_3O$ (1519.13): C 49.02, H 3.78, N 2.77; found: C 49.12, H 3.83, N 2.83.

(*R*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(2-adamantan-1-yl-4,5-dihydro-oxazol-4-ylmethyl)-3-*tert*-butyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90j**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89j** (200 mg, 0.166 mmol), [(η^4-cod)IrCl]$_2$ (56 mg, 0.083 mmol) and NaO*t*Bu (16 mg, 0.166 mmol) yielded an orange/yellow solid (120 mg, 48%, 0.080 mmol).

$[\alpha]_D^{20}$ = +39 (c = 0.128, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 6.96 (mc, 1H; imid C*H*), 6.67 (mc, 1H; imid C*H*), 5.51 (mc, 1H; NCH_2), 4.78 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.42 (mc, 1H; cod C*H*), 4.25 (mc, 1H; cod C*H*), 3.99 (mc, 1H; cod C*H*), 3.86 (mc, 2H; cod C*H* + NCH_2), 3.61 (mc, 2H; oxaz CH_2), 2.40-2.30 (m, 1H; cod CH_2), 2.30-2.00 (m, 7H, 4 x cod CH_2 + 3 x adam C*H*), 1.83 (mc, 7H; 1 x cod CH_2 + 6 x adam CH_2), 1.76 (mc, 3H; adam CH_2), 1.67 (mc, 12H; 3 x adam CH_2 + 9 x *t*Bu$_{imid}$ CH_3), 1.55 (mc, 2H; cod CH_2);

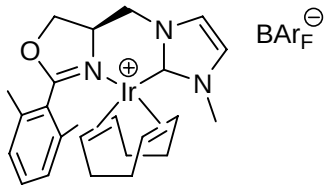
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 181.7 (O*C*N), 174.2 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 134.8 (br, 8C; BAr_F *ortho C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 122.0 (imid *C*H), 119.1 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 82.4 (cod *C*H), 77.6 (cod *C*H), 69.6 (oxaz *C*H_2), 63.4 (cod *C*H), 63.0 (oxaz *C*H), 58.9 (*t*Bu$_{imid}$ *C*), 57.6 (cod *C*H), 51.1 (N*C*H_2), 39.7 (3C; adam *C*H_2), 36.1 (adam *C*), 35.8 (3C; adam *C*H_2), 33.8 (cod CH_2), 32.4 (3C; *t*Bu$_{imid}$ CH_3), 30.8 (cod CH_2), 30.7 (cod CH_2), 28.2 (cod CH_2), 27.5 (3C; adam *C*H);

IR (KBr): $\tilde{\nu}$ = 2918w, 1609w, 1455w, 1439w, 1417w, 1356m, 1278s, 1126bs, 887w, 839w, 713w, 684w, 671w cm^{-1};

MS (FAB): *m/z* (%): 642 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{61}H_{55}BF_{24}IrN_3O$ (1505.10): C 48.68, H 3.68, N 2.79; found: C 48.73, H 3.62, N 2.80.

(*R*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazol-4-ylmethyl)-3-methyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90k**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89k** (220 mg, 0.187 mmol), [(η^4-cod)IrCl]$_2$ (63 mg, 0.094 mmol) and NaO*t*Bu (18 mg, 0.187 mmol) yielded an orange solid (198 mg, 74%, 0.138 mmol).

$[\alpha]_D^{20}$ = +48 (c = 0.121, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.72 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.34 (mc, 1H; arom C*H*), 7.10 (mc, 2H; arom C*H*), 6.71 (mc, 2H; imid C*H*), 5.12 (mc, 1H; NCH_2), 4.88 (mc, 1H; oxaz CH_2), 4.67 (mc, 1H; oxaz C*H*), 4.23 (mc, 1H; cod C*H*), 4.05 (mc, 1H; cod C*H*), 3.95 (mc, 1H; NCH_2), 3.90-3.80 (m, 6H; 1 x oxaz CH_2 + 2 x cod C*H* + 3 x NCH_3), 2.20 (s, 3H, $C_{arom}CH_3$), 2.10 (mc, 1H; cod CH_2), 1.97 (mc, 2H; cod CH_2), 1.93 (s, 3H, $C_{arom}CH_3$), 1.82 (mc, 2H; cod CH_2), 1.68 (mc, 1H; cod CH_2), 1.53 (mc, 1H; cod CH_2);

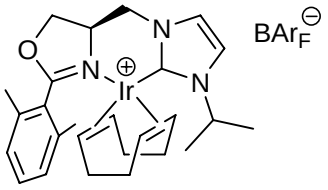
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 174.6 (O*C*N), 171.2 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 136.4 (arom *C*), 135.8 (arom *C*), 134.8 (br, 8C; BAr_F *ortho C*H), 131.6 (arom *C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 127.8 (arom *C*H), 127.5 (arom *C*H), 125.4 (arom *C*), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 123.0 (imid *C*H), 122.3 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 84.9 (cod *C*H), 83.9 (cod *C*H), 70.2 (oxaz *C*H_2), 65.3 (cod *C*H), 62.1 (oxaz *C*H), 57.6 (cod *C*H), 47.9 (N*C*H_2), 37.7 (N*C*H_3), 34.3 (cod *C*H_2), 31.0 (cod *C*H_2), 30.6 (cod *C*H_2), 28.2 (cod *C*H_2), 19.4 ($C_{arom}CH_3$), 19.1 ($C_{arom}CH_3$);

IR (KBr): $\tilde{\nu}$ = 2962w, 2081w, 2014w, 1610m, 1469w, 1356m, 1279s, 1125bs, 968w, 888w, 839w, 778w, 713w, 681w, 671w cm^{-1};

MS (FAB): *m/z* (%): 570 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{56}H_{43}BF_{24}IrN_3O$ (1432.95): C 46.94, H 3.02, N 2.93; found: C 46.62, H 3.15, N 3.03.

(*R*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazol-4-ylmethyl)-3-isopropyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90l**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89l** (285 mg, 0.245 mmol), $[(\eta^4\text{-cod})IrCl]_2$ (82 mg, 0.123 mmol) and NaO*t*Bu (24 mg, 0.245 mmol) yielded an orange solid (297 mg, 83%, 0.203 mmol).

$[\alpha]_D^{20}$ = +46 (c = 0.150, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.36 (mc, 1H; arom C*H*), 7.10 (mc, 2H; arom C*H*), 6.87 (mc, 1H; imid C*H*), 6.71 (mc, 1H; imid C*H*), 5.10 (mc, 1H; NCH_2), 4.86 (mc, 1H; oxaz CH_2), 4.78 (mc, 1H; *i*Pr C*H*), 4.62 (mc, 1H; oxaz C*H*), 4.15 (mc, 1H; cod C*H*), 4.09 (mc, 1H; cod C*H*), 3.94 (mc, 1H; NCH_2), 3.83 (mc, 1H; oxaz CH_2), 3.73 (mc, 2H; cod C*H*), 2.20 (s, 3H, $C_{arom}CH_3$), 2.16 (mc, 1H; cod CH_2), 2.06 (s, 3H, $C_{arom}CH_3$), 1.95 (mc, 4H; cod CH_2), 1.75 (mc, 1H; cod CH_2), 1.42 (d, ^3J(H,H) = 6.9 Hz, 3H; *i*Pr CH_3), 1.36 (mc, 2H; cod CH_2), 1.30 (d, ^3J(H,H) = 6.8 Hz, 3H; *i*Pr CH_3);

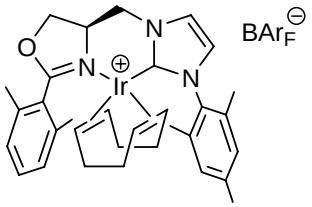
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 173.0 (OCN), 171.4 (NCN), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 136.5 (arom *C*), 135.8 (arom *C*), 134.8 (br, 8C; BAr_F *ortho* CH), 131.6 (arom CH), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 127.8 (arom CH), 127.6 (arom CH), 125.4 (arom *C*), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F CF_3), 122.9 (imid CH), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para CH), 117.4 (imid CH), 83.7 (cod CH), 83.5 (cod CH), 70.1 (oxaz CH_2), 65.5 (cod CH), 62.3 (oxaz CH), 57.6 (cod CH), 52.2 (*i*Pr CH), 47.5 (NCH_2), 35.3 (cod CH_2), 31.7 (cod CH_2), 30.1 (cod CH_2), 27.6 (cod CH_2), 25.5 (*i*Pr CH_3), 22.3 (*i*Pr CH_3), 20.5 ($C_{arom}CH_3$), 19.5 ($C_{arom}CH_3$);

IR (KBr): $\tilde{\nu}$ = 2973w, 2081w, 2015w, 1611m, 1466w, 1425w, 1356m, 1279s, 1126bs, 888w, 839w, 713w, 681w, 671w cm^{-1};

MS (FAB): *m/z* (%): 598 (100) $[M - BAr_F]^+$;

EA calcd (%) for $C_{58}H_{47}BF_{24}IrN_3O$ (1460.99): C 47.68, H 3.24, N 2.88; found: C 47.47, H 3.28, N 2.82.

(*R*)-{(η^4-1,5-cyclooctadiene)-[1-(2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazol-4-ylmethyl)-3-(2,4,6-trimethyl-phenyl)-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90m**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89m** (220 mg, 0.178 mmol), [(η^4-cod)IrCl]$_2$ (60 mg, 0.089 mmol) and NaO*t*Bu (17 mg, 0.178 mmol) yielded an orange solid (178 mg, 65%, 0.116 mmol).

$[\alpha]_D^{20}$ = +12 (c = 0.110, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.72 (mc, 8H; BAr_F *ortho* C*H*), 7.54 (mc, 4H; BAr_F para C*H*), 7.35 (mc, 1H; arom$_{oxaz}$ C*H*), 7.10 (mc, 2H; arom$_{oxaz}$ C*H*), 6.97 (mc, 2H; arom$_{imid}$ C*H*), 6.86 (mc, 1H; imid C*H*), 6.77 (mc, 1H; imid C*H*), 4.74 (mc, 1H; oxaz CH_2), 4.61 (mc, 1H; oxaz C*H*), 4.41 (mc, 1H; NCH_2), 4.26 (mc, 1H; NCH_2), 4.20 (mc, 1H; oxaz CH_2), 3.77 (mc, 1H; cod C*H*), 3.58 (mc, 1H; cod C*H*), 3.42 (mc, 1H; cod C*H*), 3.13 (mc, 1H; cod C*H*), 2.33 (s, 3H, C$_{arom,\ imid}$CH_3), 2.31 (s, 3H, C$_{arom,\ oxaz}$CH_3), 2.28 (s, 3H, C$_{arom,\ oxaz}$CH_3), 2.06 (s, 3H, C$_{arom,\ imid}$CH_3), 2.02 (s, 3H, C$_{arom,\ imid}$CH_3), 1.82-1.57 (m, 6H; cod CH_2), 1.40-1.20 (m, 2H; cod CH_2);

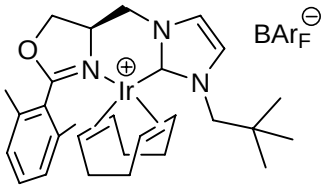
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 173.8 (O*C*N), 169.8 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 140.2 (arom$_{imid}$ *C*), 137.6 (arom$_{oxaz}$ *C*), 137.4 (arom$_{oxaz}$ *C*), 134.9 (arom$_{imid}$ *C*), 134.8 (br, 8C; BAr_F *ortho* *C*H), 134.4 (arom$_{imid}$ *C*), 134.2 (arom$_{imid}$ *C*), 132.4 (arom$_{oxaz}$*C*H), 129.8 (arom$_{imid}$*C*H), 129.7 (arom$_{imid}$*C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 128.5 (arom$_{oxaz}$*C*H), 128.4 (arom$_{oxaz}$ *C*H), 124.8 (imid *C*H), 124.7 (arom$_{oxaz}$ *C*), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 121.6 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 82.4 (cod *C*H), 81.9 (cod *C*H), 69.2 (oxaz *C*H_2), 64.8 (cod *C*H), 62.7 (oxaz *C*H), 62.4 (cod *C*H), 51.5 (N*C*H_2), 33.6 (cod *C*H_2), 31.4 (cod *C*H_2), 30.3 (cod *C*H_2), 28.4 (cod *C*H_2), 21.0 (C$_{arom\ imid}$ *C*H_3), 20.4 (C$_{arom\ oxaz}$ *C*H_3), 20.3 (C$_{arom\ oxaz}$ *C*H_3), 18.3 (C$_{arom\ imid}$ *C*H_3), 18.1 (C$_{arom\ imid}$ *C*H_3);

IR (KBr): $\tilde{\nu}$ = 2927w, 1608m, 1466w, 1355m, 1278s, 1126bs, 933w, 713w, 681w, cm^{-1};

MS (FAB): *m/z* (%): 674 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{64}H_{51}BF_{24}IrN_3O$ (1537.09): C 50.01, H 3.34, N 2.73; found: C 49.84, H 3.38, N 2.95.

(*R*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazol-4-ylmethyl)-3-(2,2-dimethyl-propyl)-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90n**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89n** (244 mg, 0.205 mmol), [(η^4-cod)IrCl]$_2$ (69 mg, 0.102 mmol) and NaO*t*Bu (20 mg, 0.205 mmol) yielded an orange solid (250 mg, 82%, 0.168 mmol).

$[\alpha]_D^{20}$ = +51 (c = 0.110, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.72 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F para C*H*), 7.34 (mc, 1H; arom C*H*), 7.10 (mc, 2H; arom C*H*), 6.95 (mc, 1H; imid C*H*), 6.80 (mc, 1H; imid C*H*), 5.06 (mc, 1H; NCH_2), 4.84 (mc, 1H; oxaz CH_2), 4.55 (mc, 1H; oxaz C*H*), 4.22 (mc, 1H; CH_2C$(CH_3)_3$), 4.06 (mc, 3H; 1 x NCH_2+ 2 x cod C*H*), 3.90 (mc, 1H; oxaz CH_2), 3.80 (mc, 1H; cod C*H*), 3.75 (mc, 1H; cod C*H*), 3.58 (mc, 1H; CH_2C$(CH_3)_3$), 2.19 (mc, 4H; 3 x $C_{arom}CH_3$ + 1 x cod CH_2), 1.93 (mc, 6H; 3 x cod CH_2 + 3 x $C_{arom}CH_3$), 1.83 (mc, 1H; cod CH_2), 1.74 (mc, 1H; cod CH_2), 1.43 (mc, 2H; cod CH_2), 0.94 (mc, 9H; CH_2C$(CH_3)_3$);

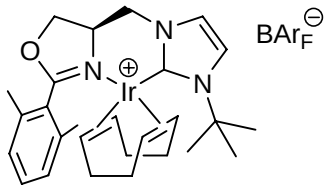
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 175.4 (O*C*N), 172.0 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 136.5 (arom *C*), 136.0 (arom *C*), 134.8 (br, 8C; BAr_F *ortho C*H), 131.7 (arom *C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 128.0 (arom *C*H), 127.7 (arom *C*H), 125.2 (arom *C*), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 122.4 (imid *C*H), 122.3 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 83.5 (cod *C*H), 82.8 (cod *C*H), 69.8 (oxaz *C*H_2), 62.9 (oxaz *C*H), 62.0 (cod *C*H), 61.2 (N*C*H_2C$(CH_3)_3$), 60.0 (cod *C*H), 48.5 (N*C*H_2), 34.6 (cod *C*H_2), 32.8 (cod *C*H_2), 31.9 (NCH_2*C*$(CH_3)_3$), 31.0 (cod *C*H_2), 30.6 (cod *C*H_2), 28.1 (NCH_2C(*C*$H_3)_3$), 19.6 (C_{arom}*C*H_3), 19.3 (C_{arom}*C*H_3);

IR (KBr): $\tilde{\nu}$ = 2965w, 2889w, 2016w, 1609m, 1468w, 1424w, 1356m, 1279s, 1126bs, 967w, 934w, 888w, 839w, 713w, 681w, 670w cm^{-1};

MS (FAB): *m/z* (%): 626 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{60}H_{51}BF_{24}IrN_3O$ (1489.06): C 48.40, H 3.45, N 2.82; found: C 48.07, H 3.33, N 2.94.

(*R*)-{(η^4-1,5-cyclooctadiene)-[1-(2-(2,6-dimethyl-phenyl)-4,5-dihydro-oxazol-4-ylmethyl)-3-*tert*-butyl-imidazolin-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90o**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89o** (256 mg, 0.217 mmol), [(η^4-cod)IrCl]$_2$ (73 mg, 0.108 mmol) and NaO*t*Bu (21 mg, 0.217 mmol) yielded an orange solid (204 mg, 64%, 0.139 mmol).

$[\alpha]_D^{20}$ = +49 (c = 0.089, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.72 (mc, 8H; BAr_F *ortho* C*H*), 7.54 (mc, 4H; BAr_F para C*H*), 7.33 (mc, 1H; arom C*H*), 7.12 (mc, 1H; arom C*H*), 7.04 (mc, 1H; imid C*H*), 7.02 (mc, 1H; arom C*H*), 6.76 (mc, 1H; imid C*H*), 5.46 (mc, 1H; NCH_2), 4.85 (mc, 2H; oxaz CH_2 + oxaz C*H*), 4.37 (mc, 1H; cod C*H*), 4.26 (mc, 1H; cod C*H*), 4.18 (mc, 1H; cod C*H*), 4.01 (mc, 1H; NCH_2), 3.88 (mc, 2H; oxaz CH_2), 3.59 (mc, 1H; cod C*H*), 2.20 (mc, 4H, 3 x $C_{arom}CH_3$ + 1 x cod CH_2), 2.10-1.80 (m, 5H; cod CH_2), 1.67 (s, 9H, C(CH_3)$_3$), 1.59 (s, 3H, $C_{arom}CH_3$), 1.38 (mc, 1H; cod CH_2), 1.32 (mc, 1H; cod CH_2);

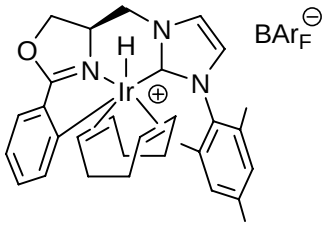
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 175.3 (O*C*N), 171.3 (N*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 136.0 (arom *C*), 135.5 (arom *C*), 134.8 (br, 8C; BAr_F *ortho* *C*H), 131.8 (arom *C*H), 128.9 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 127.8 (arom *C*H), 127.6 (arom *C*H), 125.2 (arom *C*), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 122.0 (imid *C*H), 119.6 (imid *C*H), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 80.8 (cod *C*H), 79.9 (cod *C*H), 70.2 (oxaz *C*H_2), 66.2 (cod *C*H), 62.9 (oxaz *C*H), 59.1 (*t*Bu_{imid} *C*), 56.0 (cod *C*H), 49.8 (N*C*H_2), 35.5 (cod *C*H_2), 32.5 (cod *C*H_2), 32.4 (3C; *t*Bu_{imid} *C*H_3), 29.3 (cod *C*H_2), 27.1 (cod *C*H_2), 19.7 (C_{arom}*C*H_3), 19.1 (C_{arom}*C*H_3);

IR (KBr): $\tilde{\nu}$ = 2956w, 1630w, 1611w, 1475w, 1438w, 1416w, 1356m, 1280s, 1127bs, 964w, 940w, 887w, 839w, 714w, 682w, 670w cm^{-1};

MS (FAB): *m/z* (%): 612 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{59}H_{49}BF_{24}IrN_3O$ (1475.03): C 48.04, H 3.35, N 2.85; found: C 48.04, H 3.47, N 3.06.

(*R*)-{**(**η^4-1,5-cyclooctadiene**)**-[1-(2-(phenyl)-4,5-dihydro-oxazol-4-ylmethyl)-3-(2,4,6-trimethyl-phenyl)-imidazolin-2-ylidene]iridium(III)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **90p**



Synthesis according to the metalation procedure 6.3.4 using imidazolium salt **89p** (723 mg, 0.598 mmol), [(η^4-cod)IrCl]$_2$ (200 mg, 0.299 mmol) and NaO*t*Bu (57.5 mg, 0.598 mmol) yielded a colourless solid (758 mg, 84%, 0.502 mmol).

$[\alpha]_D^{20}$ = +18.5 (c = 0.159, $CHCl_3$);

^{1}H NMR (500.1 MHz, CD_2Cl_2, 295 K) : δ = 7.72 (mc, 8H; BAr_F *ortho* C*H*), 7.56 (mc, 4H; BAr_F para C*H*), 7.34 (mc, 1H; arom$_{oxaz}$ C*H*), 7.13 (s, 1H; arom$_{imid}$ C*H*), 7.02 (mc, 3H; arom$_{oxaz}$ C*H* + arom$_{oxaz}$ C*H* + imid C*H*), 6.77 (mc, 1H; imid C*H*), 6.69 (arom$_{oxaz}$ C*H*), 6.68 (s, 1H; arom$_{imid}$ C*H*), 5.29-5.22 (m, 2H, oxaz CH_2 + oxaz C*H*), 5.02 (mc, 1H; cod C*H*), 4.89 (mc, 1H; oxaz CH_2), 4.82 (mc, 1H; cod C*H*), 4.68(mc, 1H; NCH_2), 4.41 (mc, 1H; cod C*H*), 4.12 (mc, 1H; NCH_2), 3.37 (mc, 1H; cod C*H*), 3.19 (mc, 1H; cod CH_2), 2.75 (mc, 1H; cod CH_2), 2.52 (mc, 2H; cod CH_2), 2.43 (mc, 2H; cod CH_2), 2.38 (s, 3H; $C_{arom}CH_3$), 2.15 (s, 3H; $C_{arom}CH_3$), 2.01 (mc, 1H; cod CH_2), 1.91 (mc, 1H; cod CH_2), 0.44 (s, 3H; $C_{arom}CH_3$), -14.6 (s, 1H; Ir *H*);

^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, 295 K) : δ = 182.3 (O*C*N), 161.7 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 156.4 (N*C*N), 154.1 (Ir C_{arom}), 141.3 (arom$_{oxaz}$ *C*H), 139.8 (arom$_{imid}$ *C*), 136.6 (arom$_{imid}$ *C*), 135.3 (arom$_{imid}$ *C*), 134.8 (br, 8C; BAr_F *ortho C*H), 134.1 (arom$_{imid}$ *C*), 133.9 (arom$_{oxaz}$ *C*H), 129.3 (arom$_{imid}$ *C*H), 129.0 (arom$_{imid}$ *C*H), 128.8 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 127.3 (arom$_{oxaz}$ *C*H), 124.5 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 124.4 (imid *C*H), 123.6 (arom$_{oxaz}$ *C*H), 123.5 (imid *C*H), 117.4 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F para *C*H), 89.2 (cod *C*H), 87.2 (cod *C*H), 85.2 (cod *C*H), 82.7 (cod *C*H), 77.5 (oxaz *C*H_2), 59.8 (oxaz *C*H), 55.9 (N*C*H_2), 36.9 (cod *C*H_2), 32.8 (cod *C*H_2), 28.9 (cod *C*H_2), 27.5 (cod *C*H_2), 20.8 (C_{arom}*C*H_3), 17.5 ($C_{arom}CH_3$), 15.4 (C_{arom}*C*H_3), 1 quat. C not detected;

IR (KBr): $\tilde{\nu}$ = 2933w, 1610m, 1435w, 1354s, 1277s, 1126bs, 887m, 839w, 744w, 712w, 682w, 671w cm^{-1};

MS (FAB): *m/z* (%): 646 (100) $[M - BAr_F]^+$;

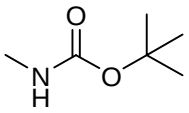
EA calcd (%) for $C_{62}H_{47}BF_{24}IrN_3O$ (1509.06): C 49.35, H 3.14, N 2.78, O 1.06; found: C 49.39, H 2.98, N 2.77, O 1.34.

6.4 Phosphine/phosphinite-*N*-heterocyclic carbene ligands

Since a detailed description of compounds **111-115**;[1] **110c**, **117c** and **118c**;[2] and **137**[3] can be found in the literature, their analytical data will not be presented here.

6.4.1 Synthesis of carbamates 117a and 117b

methyl-carbamic acid *tert*-butyl ester **117a**



A solution of $Boc_2(O)$ (24.00 g, 110 mmol) in THF (50 ml) was added to a solution of methylamine (2M, 50 ml, 100 mmol) in THF at 0°C over 10 minutes. DMAP (122 mg, 1 mmol) was added to the mixture, which was then stirred at room temperature for 19 hours. The reaction mixture was concentrated *in vacuo* to remove the solvent and the residue was dissolved in Et_2O (150 ml). The organic layer was washed with water, a saturated aqueous solution of $NaHCO_3$ and brine, dried over magnesium sulfate, before being concentrated *in vacuo* to yield a colourless oil. The crude product was purified by chromatography on silica gel eluting with a mixture of ethyl acetate and hexane (1:9) to yield a colourless oil (7.15 g, 54.5 mmol, 55%).

$\boldsymbol{R_f}$ = 0.33 (EtOAc/Hexane 1:9);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 4.41 (br, 1H; N*H*), 2.69 (s, 3H; NCH_3), 1.41 (s, 9H; C(CH_3)$_3$)

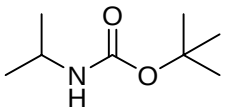
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 157.0 (O*C*ON), 79.5 (*C*(CH$_3$)$_3$), 28.8 (3C; C(*C*H$_3$)$_3$), 27.6 (NCH_3);

IR (NaCl): $\tilde{\nu}$ = 3357 mbr, 2976m, 2933m, 1696sbr, 1531m, 1456w, 1419w, 1391w, 1366m, 1277m, 1250m, 1175s, 954w, 868w, 782 cm^{-1};

MS (FAB): *m/z* (%): 132 (10) $[M + H]^+$, 76 (63), 57 (100), 41 (44);

EA calcd (%) for $C_6H_{13}NO_2$ (131.17): C 54.94, H 9.99, N 10.68; found: C 54.92, H 9.79, N 7.04, O 10.51.

isopropyl-carbamic acid *tert*-butyl ester **117b**



Synthesis according to the previous general procedure using diethylamine **116b** (1.00 g, 16.92 mmol), $Boc_2(O)$ (4.06 g, 18.61 mmol) and DMAP (20 mg, 0.17 mmol) yielded a white solid (2.21 g, 13.77 mmol, 74%).

$\boldsymbol{R_f}$ = 0.48 (EtOAc/Hexane 1:9);

m.p. 69-71°C;

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 4.31 (br, 1H; N*H*), 3.71 (mc, 1H; C*H*$(CH_3)_2$), 1.41 (s, 9H; C(C*H*$_3$)$_3$), 1.11 (mc, 3H; CH(C*H*$_3$)$_2$), 1.09 (mc, 3H; CH(C*H*$_3$)$_2$);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 155.6 (N*C*OO), 79.3 (O*C*$(CH_3)_3$), 43.0 (*C*$(CH_3)_2$), 28.8 (C(*C*H$_3$)$_3$), 23.5 (CH(*C*H$_3$)$_2$);

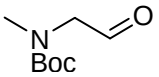
IR (KBr): $\tilde{\nu}$ = 3346m, 2978m, 2935m, 1683s, 1539m, 1459m, 1367m, 1256s, 1174s, 1078s, 938w, 886w, 841w, 778w, 753w, 643m, 461w, 424w cm^{-1};

MS (FAB): *m/z* (%): 160 (100) $[M + H]^+$, volatile compound difficult to measure;

EA calcd (%) for $C_8H_{17}NO_2$ (159.23): C 60.35, H 10.76, N 8.80, O 20.10; found: C 60.41, H 10.56, N 8.64, O 20.28.

6.4.2 Synthesis of aldehydes 110a and 110b

methyl-(2-oxo-ethyl)-carbamic acid *tert*-butyl ester **110a**



A solution of carbamate **117a** (10.05 g, 76.6 mmol) in DMF (100 ml) at 0°C was added to a suspension of KH (3.38 g, 84.3 mmol, free of mineral oil) in DMF at 0°C over ½ hour. The reaction mixture was stirred at room temperature until the gas evolution had ceased (typically 2 hours). 3,3-Dimethylallylbromide (13.7 g, 91.9 mmol) was then added and the resultant mixture was stirred at room temperature for a further one hour. The solution was quenched with a saturated aqueous solution of $NaHCO_3$ (100 ml) and water (100 ml), then the mixture extracted three times with Et_2O (3 x 100 ml). The combined organic layers were dried over anhydrous magnesium sulfate and concentrated *in vacuo* to yield a colourless oil (11.56 g). Since **118a** was not stable on silica gel, the crude product was used for the next step without purification.

Crude olefin **118a** was dissolved in a mixture of CH_2Cl_2 and MeOH (3:1, 500 ml). The mixture was cooled to -78°C and a ozone was bubbled into the reaction mixture until TLC analysis indicated that no starting material remained (typically ½ hour). The reaction mixture was warmed to room temperature and reduced with dimethyl sulfide (7.21 g, 116 mmol). The solvent and excess dimethyl sulfide were removed under high vacuum. The crude product was purified by chromatography on silica gel eluting with a mixture of ethyl acetate and hexane (3:7) to yield a colorless oil (6.38 g, 36.8 mmol, 48% over two steps).

$\boldsymbol{R_f}$ = 0.40 (EtOAc/Hexane 3:7);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 9.56 (s, 1H; C*H*O), 3.99-3.87 (m, 2H; NCH_2), 2.93-2.88 (m, 3H; NCH_3), 1.44-1.38 (m, 9H; C(CH_3)$_3$);

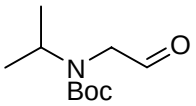
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 199.0 (*C*HO), 156.5 (N*C*OO), 155.8 (N*C*OO), 81.1 (*C*(CH$_3$)$_3$), 80.9 (*C*(CH$_3$)$_3$), 59.6 (N*C*H$_2$), 59.1 (N*C*H$_2$), 36.2 (N*C*H$_3$), 28.6 (br, 3C; C(*C*H$_3$)$_3$), two sets of signals were observed due to amide conformers;

IR (NaCl): $\tilde{\nu}$ = 2976m, 2933m, 1734m, 1695s, 1481m, 1456m, 1392m, 1297w, 1242m, 1158s, 1056w, 929w, 878w, 775w cm^{-1};

MS (FAB): *m/z* (%): 174 (37), $[M + H]^+$, 118 (100), 57 (88);

elemental analysis calcd (%) for $C_8H_{15}NO_3$ (173.21): C 55.47, H 8.73, N 8.09; found: C 54.73, H 8.44, N 8.09.

isopropyl-(2-oxo-ethyl)-carbamic acid *tert*-butyl ester **110b**



Synthesis according to the previous general procedure using carbamate **117b** (4.83 g, 30.4 mmol), KH (1.34 g, 33.4 mmol), 3,3-dimethylallylbromide (5.97 g, 40.1 mmol) and dimethyl sulfide (2.52 g, 40.6 mmol) yielded a white solid (1.790 g, 8.89 mmol, 30%).

$\boldsymbol{R_f}$ = 0.54 (EtOAc/Hexane 3:7);

m.p. 36-37°C;

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 9.48 (br, 1H; C*H*O), 4.50 (br, 0.64H; C*H*(CH$_3$)$_2$), 4.23 (br, 0.36H; C*H*(CH$_3$)$_2$), 1.60-1.30 (m, 9H; C(CH_3)$_3$), 1.07 (mc, 6H; CH(CH_3)$_2$).

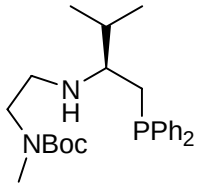
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ =

δ = 200.2 (*C*HO), 155.8 (N*C*OO), 154.8 (N*C*OO), 80.8 (*C*(CH$_3$)$_3$), 80.6 (*C*(CH$_3$)$_3$), 51.4 (N*C*H$_2$), 51.1 (N*C*H$_2$), 47.4 (*C*H(CH$_3$)$_2$), 46.0 (*C*H(CH$_3$)$_2$), 28.4 (br, 3C; C(*C*H$_3$)$_3$), 21.1 (CH(*C*H$_3$)$_2$), 20.7 (CH(*C*H$_3$)$_2$), two sets of signals were observed due to amide conformers;

IR (KBr): $\tilde{\nu}$ = 2978m, 2805w, 2709w, 1739m, 1696s, 1437m, 1398m, 1366m, 1295m, 1253m, 1219m, 1169s, 1108m, 1019m, 900m, 857w, 823w, 773m, 680w, 456w cm^{-1};
MS (FAB): *m/z* (%): 202 (10) $[M + H]^+$, 172 (39), 146 (21), 116 (34), 72 (60), 57 (100);
EA calcd (%) for $C_{10}H_{19}NO_3$ (201.26): C 59.68, H 9.51, N 6.96, O 23.85; found: C 59.61, H 9.37, N 7.05, O 23.96.

6.4.3 Synthesis of phosphines 119a-c

(*S*)-(2-{1-[(diphenylphosphanyl)-methyl]-2-methyl-propylamino}-ethyl)-methyl-carbamic acid *tert*-butyl ester **119a**



A solution of aldehyde **110a** (421 mg, 2.43 mmol) in 1,2-dichlorethane (5 ml) was added to a solution of amino-phosphine **111** (600 mg, 2.21 mmol) and $NaHB(OAc)_3$ (933 mg, 4.42 mmol) in 1,2-dichlorethane (3 ml) at room temperature. The reaction mixture was stirred at room temperature for four hours and quenched with a saturated aqueous solution of $NaHCO_3$ (10 ml). The organic layer was separated and the aqueous layer was extracted three times with CH_2Cl_2 (3 x 10 ml). The combined organic layers were dried over magnesium sulfate and concentrated *in vacuo* to yield a yellow oil. The crude product was purified by chromatography on silica gel eluting with a mixture of ethyl acetate and hexane (4:6) to yield a colourless oil (700 mg, 1.63 mmol, 74%).

R_f = 0.56 (EtOAc/Hexane 4:6);
$[\alpha]_D^{20}$ = +52.2 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.49-7.43 (m, 2H; arom C*H*), 7.43-7.38 (mc, 2H; arom C*H*), 7.37-7.27 (m, 6H; arom C*H*), 3.19 (br, 2H; NCH_2), 2.82 (s, 3H; CH_3), 2.71-2.58 (br, 2H; NCH_2), 2.36 (mc, 1H; PCH_2CH), 2.22 (br, 1H; PCH_2), 2.25-1.85 (br, 2H; 1 x PCH_2 + 1 x $CCH(CH_3)_2$), 1.44 (br, 9H; $OC(CH_3)_3$), 0.87 (d, ^3J(H;H) = 6.8 Hz, 3H; $NCH(CH_3)_2$), 0.83 (d, ^3J(H;H) = 7.8 Hz, 3H; $NCH(CH_3)_2$),1 N*H* not detected;
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 155.9 (br, N*C*O), 139.6 (br, arom *C*), 138.4 (br, arom *C*), 133.4 (arom *C*H), 133.2 (arom *C*H), 132,7 (br, arom *C*H), 132.6 (br, arom *C*H), 129.0 (arom *C*H), 128.7-128.4 (5C; arom *C*H), 70.4 ($OC(CH_3)_3$), 60.6 (br; PCH_2CH), 49.2

(N*C*H_2), 45.9 (N*C*H_2), 35.2 (N*C*H_3), 30.8 (br, C*C*H(CH_3)$_2$), 30.6 (br, P*C*H_2), 28.6 (3C; C(*C*H_3)$_3$), 18.4 (br, CCH(*C*H_3)$_2$), 17.5 (CCH(*C*H_3)$_2$);

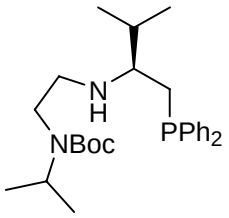
^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 295 K) : δ = -21.2 (s);

IR (NaCl): $\tilde{\nu}$ = 3056w, 2961m, 1694s, 1478m, 1433w, 1392m, 1368w, 1247w, 1155m, 879w, 741w, 696w cm^{-1};

MS (FAB): *m/z* (%):429 (100) $[M + H]^+$, 445 (18) oxidation during measurement;

EA calcd (%) for $C_{25}H_{37}N_2O_2P$ (428.55): C 70.07, H 8.70, N 6.54, O 7.47; found: C 69.83, H 8.52, N 6.60, O 7.55.

(*S*)-(2-{1-[(diphenylphosphanyl)-methyl]-2-methyl-propylamino}-ethyl)-isopropyl-carbamic acid *tert*-butyl ester **119b**



Synthesis according to the previous general procedure using aldehyde **110b** (250 mg, 1.24 mmol), amino-phosphine **111** (306 mg, 1.13 mmol) and NaHB(OAc)$_3$ (526 mg, 2.48 mmol) yielded a colourless oil which crystallised on standing (413 mg, 0.904 mmol, 80%).

R_f = 0.69 (EtOAc/Hexane 1:1);

m.p. 51-52°C;

$[\alpha]_D^{20}$ = +60.4 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.46 (mc, 2H; arom C*H*), 7.40 (mc, 2H; arom C*H*), 7.36-7.27 (br, 6H; arom C*H*), 4.40-3.80 (br, 1H; NC*H*(CH_3)$_2$), 3.30-2.90 (br, 2H; NCH_2), 2.65 (br, 2H; NCH_2), 2.40 (br, 1H; PCH_2C*H*), 2.27 (br, 1H; PCH_2), 2.15-1.85 (br, 2H; 1 x PCH_2 + 1 x CC*H*(CH_3)$_2$), 1.42 (br, 9H; OC(CH_3)$_3$), 1.07 (br, 6H; NCH(CH_3)$_2$), 0.89 (br, 3H; CCH(CH_3)$_2$), 0.84 (br, 3H; CCH(CH_3)$_2$), 1 N*H* not detected;

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 138.3 (d, ^1J(P,C) = 12.6 Hz; arom *C*), 133.4 (d, ^2J(P,C) = 19.3 Hz, 2C; arom *C*H), 132.6 (d, ^2J(P,C) = 17.5 Hz, 2C; arom *C*H), 128.8-128.3 (5C; arom *C*H), 60.5 (br; PCH_2*C*H), 47.9 (N*C*H_2), 46.5 (br, N*C*H(CH_3)$_2$), 42.8 br, (N*C*H_2), 30.8 (d, ^1J(P,C) = 7.0 Hz; P*C*H_2), 30.5 (br, C*C*H(CH_3)$_2$), 28.6 (3C; C(*C*H_3)$_3$), 20.9 (2C; NCH(*C*H_3)$_2$), 18.6 (CCH(*C*H_3)$_2$), 17.5 (CCH(*C*H_3)$_2$), 1 arom *C* and 1 quat *C*(CH_3)$_3$ not detected;

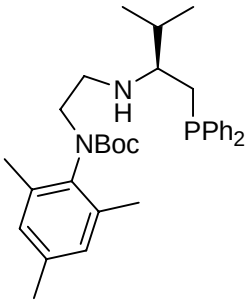
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$, 295 K) : δ = -21.1 (br);

IR (KBr): $\tilde{\nu}$ = 3068w, 2967m, 2872m, 2815m, 1593s, 1472m, 1412m, 1367m, 1343m, 1299m, 1250w, 1169m, 1122m, 1089w, 998w, 905w, 836w, 744m, 695m, 508w cm^{-1};

MS (FAB): *m/z* (%): 457 (100) $[M + H]^+$, 473 (17) oxidation during measurement;

EA calcd (%) for $C_{27}H_{41}N_2O_2P$ (456.60): C 71.02, H 9.05, N 6.14, O 7.01; found: C 70.91, H 8.97, N 6.22, O 7.03.

(*S*)-(2-{1-[(diphenylphosphanyl)-methyl]-2-methyl-propylamino}-ethyl)-(2,4,6-trimethyl-phenyl)-carbamic acid *tert*-butyl ester **119c**



Synthesis according to the previous general procedure using aldehyde **110c** (675 mg, 2.43 mmol), amino-phosphine **111** (600 mg, 2.21 mmol) and $NaHB(OAc)_3$ (937 mg, 4.42 mmol) yielded a colourless oil (961 mg, 1.80 mmol, 82%).

R_f = 0.43 (EtOAc/Hexane 2:8);

$[\alpha]_D^{20}$ = +30.5 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.47-7.24 (m, 10H; $arom_{phenyl}$ C*H*), 6.88-6.83 (m, 2H; $arom_{mesityl}$ C*H*), 3.55-3.25 (m, 2H; NCH_2), 2.76-2.62 (m, 2H; NCH_2), 2.35 (mc, 1H; PCH_2CH), 2.28-2.24 (m, 3H; mesityl CH_3), 2.24-2.17 (m, 1H; PCH_2), 2.16-2.09 (m, 6H; mesityl CH_3), 2.02-1.87 (m, 2H; 1 x PCH_2 + 1 x CC$H(CH_3)_2$), 1.48 (s, 3H; $OC(CH_3)_3$), 1.30 (s, 6H; $OC(CH_3)_3$), 0.84 (m, 6H; $CCH(CH_3)_2$), 1 N*H* not detected;

$^{13}C\{^{1}H\}$ NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 139.7 (arom), 139.6 (arom), 138.3 (arom), 138.2 (arom), 138.0 (arom), 136.8 (arom), 136.5 (br, arom), 135.9 (arom), 135.8 (arom), 135.3 (br, arom), 133.4 (arom), 133.29 (arom), 133.28 (arom), 133.1 (arom), 132.8 (arom), 132.7 (arom), 132.6 (arom), 132.4 (arom), 129.4 (arom), 129.3 (arom), 129.2-128.3 (m, arom), 60.8 (br; PCH_2CH), 60.5 (d, ^2J(P,C) = 12.6 Hz; PCH_2CH), 51.0 (NCH_2), 49.9 (br, NCH_2), 46.6 (br, NCH_2), 30.8 (d, ^1J(P,C) = 7.0 Hz; PCH_2), 30.7 (d, ^1J(P,C) = 7.3 Hz; PCH_2), 30.6 (br, $CCH(CH_3)_2$), 30.5 (br, $CCH(CH_3)_2$), 28.6 (3C; $C(CH_3)_3$), 28.4 (3C; $C(CH_3)_3$), 21.0

(mesityl *C*H_3), 18.6 (*C*H_3), 18.31 (*C*H_3), 18.29 (*C*H_3), 18.1 (*C*H_3), 17.8 (*C*H_3), 17.3 (*C*H_3); two sets of signal corresponding to the amide rotamers, 2 quat *C*$(CH_3)_3$ not detected;

^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 295 K) : δ = -21.2 (br), -21.3 (s);

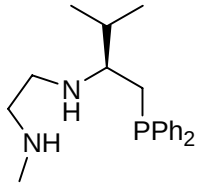
IR (KBr): $\tilde{\nu}$ = 3054m, 2959m, 2927m, 2867m, 1695s, 1479m, 1370m, 1310m, 1254m, 1150m, 1030w, 994w, 855w, 741m, 696m cm^{-1};

MS (FAB): *m/z* (%): 533 (100) $[M + H]^+$, 549 (38) oxidation during measurement;

EA calcd (%) for $C_{33}H_{45}N_2O_2P_1$ (532.70): C 74.41, H 8.51, N 5.26, O 6.01; found: C 74.43, H 8.49, N 5.29, O 6.12.

6.4.4 Synthesis of diamines 120a-c

(*S*)-*N*-{1-[(diphenylphosphanyl)-methyl]-2-methyl-propyl}-*N*'-methyl-ethane-1,2-diamine **120a**



TFA (6.00 g, 53.0 mmol) was added to a solution of phosphine **119a** (450 mg, 1.05 mmol) in CH_2Cl_2 (15 ml) at 0°C. The reaction mixture was stirred at room temperature for 20 hours. The reaction mixture was quenched with water (15 ml) and 5M NaOH until pH > 10. The organic layer was separated and the aqueous layer was extracted two times with CH_2Cl_2 (2 x 15 ml). The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated *in vacuo* to yield a yellow oil (327 mg, 0.99 mmol, 95%) of >95% purity as judged by ^{1}H-NMR analysis.

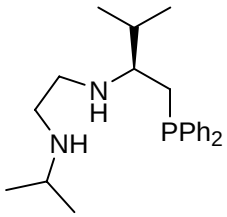
$[\alpha]_D^{20}$ = +71.8 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.49-7.27 (m, 10H; arom C*H*), 2.78-2.54 (m, 4H; NCH_2), 2.43 (s, 3H; CH_3), 2.37 (mc, 1H; PCH_2CH), 2.23 (mc, 1H; PCH_2), 2.03-1.86 (m, 2H; PCH_2 + CC$H(CH_3)_2$), 0.87 (d, ^3J(H,H) = 6.8 Hz, 3H; CCH(CH_3)$_2$), 0.84 (d, ^3J(H,H) = 6.9 Hz, 3H; CCH(CH_3)$_2$), 2 N*H* not detected;

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 139.8 (d, ^1J(P,C) = 12.0 Hz; arom *C*), 138.6 (d, ^1J(P,C) = 12.8 Hz; arom *C*), 133.6 (d, ^2J(P,C) = 19.2 Hz, 2C; arom *C*H), 132.8 (d, ^2J(P,C) = 18.3 Hz, 2C; arom *C*H), 129.3 (arom *C*H), 129.1-128.6 (5C; arom *C*H), 60.7 (d, ^2J(P,C) = 12.7 Hz; PCH_2CH), 51.7 (NCH_2), 46.4 (NCH_2), 36.1 (NCH_3), 31.2-31.0 (m, 2C; PCH_2 + C$CH(CH_3)_2$), 19.0 (CCH(*C*H_3)$_2$), 17.5 (CCH(*C*H_3)$_2$);

IR (NaCl): $\tilde{\nu}$ = 3055w, 2954s, 2887m, 2792m, 1686m, 1585w, 1471m, 1435m, 1381w, 1305w, 1271w, 1198m, 1131m, 1027w, 997w, 910w, 827w, 741s, 696s cm^{-1};
MS (FAB): *m/z* (%):329 (100) $[M + H]^+$, 345 (17) oxidation during measurement;
EA (%) for $C_{20}H_{29}N_2P$ (328.44): C 73.14, H 8.90, N 8.53; found: C 69.56, H 8.36, N 8.17.

(*S*)-*N*-{1-[(diphenylphosphanyl)-methyl]-2-methyl-propyl}-*N*'-isopropyl-ethane-1,2-diamine **120b**

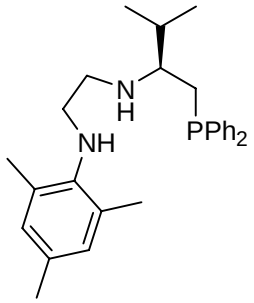


Synthesis according to the previous general procedure using phosphine **119b** (358 mg, 0.784 mmol) and TFA (4.47 g, 39.2 mmol) yielded a yellow oil (278 mg, 0.780 mmol, 99%) of >95% purity as judged by ^{1}H-NMR analysis.

$[\alpha]_D^{20}$ = +60.5 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.45 (mc, 2H; arom C*H*), 7.40 (mc, 2H; arom C*H*), 7.31 (mc, 6H; arom C*H*), 2.78 (mc, 1H; NC*H*$(CH_3)_2$), 2.69 (mc, 2H; NCH_2), 2.59 (mc, 2H; NCH_2), 2.38 (mc, 1H; PCH_2CH), 2.21 (mc, 1H; PCH_2), 1.99 (mc, 1H; PCH_2), 1.93 (mc, 1H; CC*H*$(CH_3)_2$), 1.07 (mc, 6H; NCH(CH_3)$_2$), 0.87 (d, ^3J(H,H) = 6.9 Hz, 3H; CCH(CH_3)$_2$), 0.83 (d, ^3J(H,H) = 6.9 Hz, 3H; CCH(CH_3)$_2$), 2 N*H* not detected;
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 139.6 (d, ^1J(P,C) = 12.3 Hz; arom *C*), 138.5 (d, ^1J(P,C) = 13.1 Hz; arom *C*), 133.3 (d, ^2J(P,C) = 18.3 Hz, 2C; arom *C*H), 132.6 (d, ^2J(P,C) = 18.4 Hz, 2C; arom *C*H), 128.9 (arom *C*H), 128.7-128.2 (5C; arom *C*H), 60.3 (d, ^2J(P,C) = 12.9 Hz; PCH_2CH), 49.0 (NC*H*$(CH_3)_2$), 47.2 (NCH_2), 46.7 (NCH_2), 30.7 (d, ^1J(P,C) = 11.9 Hz; PCH_2), 30.7 (C*C*H$(CH_3)_2$), 22.8 (NCH(*C*H_3)$_2$), 22.6 (NCH(*C*H_3)$_2$), 18.6 (CCH(*C*H_3)$_2$), 17.3 (CCH(*C*H_3)$_2$);
^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 295 K) : δ = -20.9 (s);
IR (NaCl): $\tilde{\nu}$ = 3056w, 2959m, 1683m, 1589w, 1469m, 1435m, 1380w, 1266w, 1178m, 1133m, 1027w, 831w, 739m, 696m cm^{-1};
MS (FAB): *m/z* (%): 357 (100) $[M + H]^+$, 373 (19) oxidation during measurement;
EA calcd (%) for $C_8H_{16}ClNO_2$ (356.49): C 74.12, H 9.33, N 7.86; found: C 72.64, H 9.25, N 7.96.

(*S*)-*N*-{1-[(diphenylphosphanyl)-methyl]-2-methyl-propyl}-*N*'-(2,4,6-trimethyl-phenyl)-ethane-1,2-diamine **120c**



Synthesis according to the previous general procedure using phosphine **119c** (184 mg, 0.346 mmol) and TFA (1.97 g, 17.3 mmol) yielded a yellow oil (122 mg, 0.284 mmol, 82%) of >95% purity as judged by ^{1}H-NMR analysis.

$[\alpha]_D^{20}$ = +54.7 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.48 (mc, 2H; $arom_{phenyl}$ C*H*), 7.42 (mc, 2H; $arom_{phenyl}$ C*H*), 7.38-7.27 (m, 6H; $arom_{phenyl}$ C*H*), 6.81 (mc, 2H; $arom_{mesityl}$ C*H*), 2.99 (mc, 1H; NCH_2), 2.88 (mc, 1H; NCH_2), 2.76 (mc, 1H; NCH_2), 2.70 (mc, 1H; NCH_2), 2.44 (mc, PCH_2CH; 1H), 2.30-2.20 (m, 10H; 1 x PCH_2 + 6 x $mesityl_{ortho}$ CH_3 + 3 x $mesityl_{para}$ CH_3), 2.06 (mc, PCH_2; 1H), 1.99 (mc, C$H(CH_3)_2$; 1H), 0.93 (d, ^{3}J(H,H) = 6.8 Hz, 3H; C$H(CH_3)_2$), 0.87 (d, ^{3}J(H,H) = 6.9 Hz, 3H; C$H(CH_3)_2$), 2 N*H* not detected;

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 144.0 ($arom_{mesityl}$ C), 139.5 (d, ^{1}J(P,C) = 13.8 Hz; $arom_{phenyl}$ *C*), 138.6 (d, ^{1}J(P,C) = 14.8 Hz; $arom_{phenyl}$ *C*), 133.3 (d, ^{2}J(P,C) = 19.3 Hz, 2C; $arom_{phenyl}$ *C*H), 132.7 (d, ^{2}J(P,C) = 19.7 Hz, 2C; $arom_{phenyl}$ *C*H), 130.9 ($arom_{mesityl}$ *C*), 129.6-129.4 (4C; 2 x $arom_{mesityl}$ *C* + 2 x $arom_{mesityl}$ *C*H), 128.9 ($arom_{phenyl}$ *C*H), 128.7-128.4 (5C; arom *C*H), 60.6 (d, ^{2}J(P,C) = 13.1 Hz; PCH_2CH), 49.0 (br, NCH_2), 48.1 (NCH_2), 30.9 (d, ^{1}J(P,C) = 7.4 Hz; PCH_2), 30.7 (br, *C*H$(CH_3)_2$), 20.7 (mesityl *C*H_3), 18.7 (2C; mesityl *C*H_3), 18.3 (CH(*C*$H_3)_2$), 17.7 (CH(*C*$H_3)_2$);

^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 295 K) : δ = -21.3 (s);

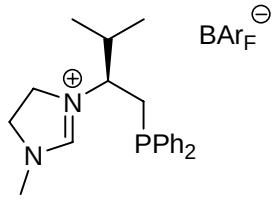
IR (NaCl): $\tilde{\nu}$ = 3353w, 3056w, 2955m, 1683w, 1586w, 1482m, 1436m, 1375w, 1304w, 1236w, 1106w, 1027w, 853w, 739m, 698m cm^{-1};

MS (FAB): *m/z* (%):433 (100) $[M + H]^+$, 449 (15) oxidation during measurement;

EA calcd (%) for $C_{28}H_{37}N_2P$ (432.59): C 77.74, H 8.62, N 6.48; found: C 76.36, H 8.13, N 6.77.

6.4.5 Synthesis of imidazolium salts 109a-c

(*S*)-1-{1-[(diphenylphosphanyl)-methyl]-2-methyl-propyl}-3-methyl-4,5-dihydro-3*H*-imidazol-1-ium-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **109a**



A solution of diamine **120a** (217 mg, 0.661 mmol) and NH_4BF_4 (77 mg, 0.726 mmol) in triethylorthoformate (4.0 ml, 26.0 mmol) was heated at 110°C for 1 hour. The crude oil was decanted and dissolved in CH_2Cl_2 (10 ml). $NaBAr_F$ (586 mg, 0.661 mmol) was added to the mixture, which was then stirred for 15 minutes. The solution was filtered and concentrated *in vacuo* to remove the solvent. The crude product was purified by chromatography on silica gel under inert atmosphere eluting with CH_2Cl_2 to yield a white solid (409 mg, 0.340 mmol, 51%).

m.p. 97-98°C;

$[\alpha]_D^{20}$ = +26.5 (c = 1.00, $CHCl_3$);

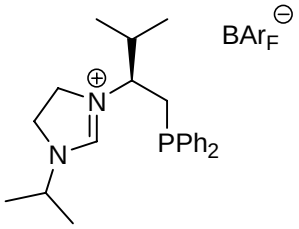
^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.69 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F *para* C*H*), 7.45-7.25 (m, 10H; arom C*H*), 7.05 (s, 1H; NC*H*N), 3.65-3.43 (m, 3H; NCH_2), 3.43-3.15 (m, 2H; 1 x NCH_2 + 1 x PCH_2CH), 2.87 (s, 3H; NCH_3), 2.57 (mc, 1H; PCH_2), 2.27 (mc, 1H; PCH_2), 1.78 (mc, 1H; CHC$H(CH_3)_2$), 0.99 (d, ^3J(H,H) = 6.6 Hz, 3H; $CH_2CH(CH_3)_2$), 0.79 (d, ^3J(H,H) = 6.6 Hz, 3H; $CH_2CH(CH_3)_2$);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 162.0 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 156.0 (N*C*HN), 136.2 (d, ^1J(P,C) = 10.2 Hz, 1C; arom *C*), 135.2 (br, 8C; BAr_F *ortho C*H), 134.4 (d, ^1J(P,C) = 9.8 Hz, 1C; arom *C*), 133.3 (d, *J*(P,C) = 20.2 Hz, 2C; arom *C*H), 132.8 (d, *J*(P,C) = 19.5 Hz, 2C; arom *C*H), 130.59 (arom *C*H), 130.57 (arom *C*H), 129.7 (d, *J*(P,C) = 7.4 Hz, 2C; arom *C*H), 129.6 (d, *J*(P,C) = 7.7 Hz, 2C; arom *C*H), 129.3 (qq, ^2J(F,C) = 31.1 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.9 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 117.9 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F *para C*H), 65.8 (d, ^2J(P,C) = 14.8 Hz, 1C; PCH_2CH), 50.0 (N*C*H_2), 46.0 (d, ^4J(P,C) = 3.5 Hz, 1C; NCH_2), 35.2 (N*C*H_3), 32.2 (d, ^3J(P,C) = 6.7 Hz, 1C; $CH_2CH(CH_3)_2$), 29.3 (d, ^1J(P,C) = 15.2 Hz, 1C; PCH_2), 19.6 ($CH_2CH(CH_3)_2$), 19.4 ($CH_2CH(CH_3)_2$);

^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 295 K) : δ = -25.4 (s);

IR (KBr): $\tilde{\nu}$ = 3076w, 2975w, 1659m, 1612w, 1526w, 1467w, 1435w, 1358s, 1280s, 1123s, 930w, 889m, 838w, 748w, 711w, 674m, 501w, 450w cm^{-1};
MS (FAB): *m/z* (%): 339 (100) $[M - BAr_F]^+$, 355 (29) oxidation during measurement;
EA calcd (%) for $C_{53}H_{40}BF_{24}N_2P$ (1202.64): C 52.93, H 3.35, N 2.33; found: C 53.14, H 3.34, N 2.36.

(*S*)-1-{1-[(diphenylphosphanyl)-methyl]-2-methyl-propyl}-3-isopropyl-4,5-dihydro-3*H*-imidazol-1-ium-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **109b**



Synthesis according to the previous general procedure using diamine **120b** (167 mg, 0.468 mmol), NH_4BF_4 (49 mg, 0.468 mmol), triethylorthoformate (2.0 ml, 13.0 mmol) and $NaBAr_F$ (414 mg, 0.468 mmol) yielded a white solid (460 mg, 0.373 mmol, 80%).

m.p. 98-99°C;
$[\alpha]_D^{20}$ = +25.1 (c = 1.00, $CHCl_3$);
^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 4H; BAr_F *para* C*H*), 7.44-7.35 (m, 10H; arom C*H*), 7.13 (s, 1H; NC*H*N), 3.70-3.55 (m, 4H; 3 x NCH_2 + 1 x $NCH(CH_3)_2$), 3.43 (mc, 1H; $NCH(CH_3)_2$), 3.24 (mc, 1H; PCH_2CH), 2.62 (mc, 1H; PCH_2), 2.26 (mc, 1H; PCH_2), 1.79 (mc, 1H; $CHCH(CH_3)_2$), 1.21 (m, 6H; $NCH(CH_3)_2$), 0.98 (d, ^3J(H,H) = 6.6 Hz, 3H; $CH_2CH(CH_3)_2$), 0.79 (d, ^3J(H,H) = 6.4 Hz, 3H; $CH_2CH(CH_3)_2$);
^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 161.8 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 153.8 (N*C*HN), 135.9 (d, ^1J(P,C) = 9.8 Hz, 1C; arom *C*), 134.9 (br, 8C; BAr_F *ortho C*H), 135.0 (d, ^1J(P,C) = 9.3 Hz, 1C; arom *C*), 132.8 (d, *J*(P,C) = 11.4 Hz, 2C; arom *C*H), 132.7 (d, *J*(P,C) = 11.2 Hz, 2C; arom *C*H), 130.5 (arom *C*H), 130.2 (arom *C*H), 129.6 (d, *J*(P,C) = 7.4 Hz, 2C; arom *C*H), 129.4 (d, *J*(P,C) = 7.5 Hz, 2C; arom *C*H), 129.0 (qq, ^2J(F,C) = 31.1 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.7 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 117.5 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F *para C*H), 65.3 (d, ^2J(P,C) = 11.9 Hz, 1C; PCH_2CH), 51.4 ($NCH(CH_3)_2$), 45.8 (NCH_2), 44.8 (d, ^4J(P,C) = 4.1 Hz, 1C; NCH_2), 31.8

(d, ^{3}J(P,C) = 6.1 Hz, 1C; $CH_2CH(CH_3)_2$), 28.9 (d, ^{1}J(P,C) = 13.9 Hz, 1C; PCH_2), 20.57 ($NCH(CH_3)_2$), 20.47 ($NCH(CH_3)_2$), 19.4 ($CH_2CH(CH_3)_2$), 19.0 ($CH_2CH(CH_3)_2$);

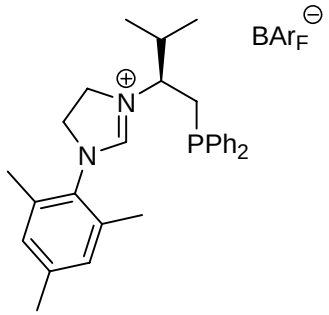
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$, 295 K) : δ = -22.6 (s);

IR (KBr): $\tilde{\nu}$ = 3072w, 2978w, 1643m,1470w, 1434w, 1358s, 1279s, 1128s, 930w, 890w, 838w, 744w, 708m, 674m, 506w, 450w cm^{-1};

MS (FAB): *m/z* (%): 367 (100) $[M - BAr_F]^+$, 383 (37) oxidation during measurement;

EA calcd (%) for $C_{55}H_{44}BF_{24}N_2P$ (1230.70): C 53.68, H 3.60, N 2.28; found: C 53.49, H 3.64, N 2.36.

(*S*)-1-{1-[(diphenylphosphanyl)-methyl]-2-methyl-propyl}-3-(2,4,6-trimethyl-phenyl)-4,5-dihydro-3*H*-imidazol-1-ium-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **109c**



Synthesis according to the previous general procedure using diamine **120c** (150 mg, 0.347 mmol), NH_4BF_4 (36 mg, 0.347 mmol), triethylorthoformate (4.0 ml, 26.0 mmol) and $NaBAr_F$ (307 mg, 0.347 mmol) yielded a colourless oil (218 mg, 0.166 mmol, 48%).

$[\alpha]_D^{20}$ = +63.2 (c = 1.00, $CHCl_3$);

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.50 (mc, 4H; BAr_F *para* C*H*), 7.48-7.39 (m, 5H; 3 x $arom_{phenyl}$ C*H* + 2 x $arom_{mesityl}$ C*H*), 7.38-7.30 (m, 6H; 1 x NC*H*N + 5 x $arom_{phenyl}$ C*H*), 6.98 (br, 2H; $arom_{phenyl}$ C*H*), 4.25-4.06 (m, 3H; 3 x NCH_2), 3.96 (mc, 1H; NCH_2), 3.18 (mc, 1H; PCH_2CH), 2.78 (mc, 1H; PCH_2), 2.40-2.25 (br, 6H; 2 x CH_3), 2.15 (m, 2H; 1 x CH_3 + 1 x PCH_2), 1.93 (mc, 1H; $NCH(CH_3)_2$), 1.00 (d, ^{3}J(H,H) = 6.6 Hz, 3H; $NCH(CH_3)_2$), 0.91 (d, ^{3}J(H,H) = 6.4 Hz, 3H; $NCH(CH_3)_2$);

$^{13}C\{^{1}H\}$ NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 161.8 (q, ^{1}J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 156.9 (N*C*HN), 142.1 ($arom_{mesityl}$ *C*) 135.7 (d, ^{1}J(P,C) = 7.9 Hz, 1C; $arom_{phenyl}$ *C*), 134.9 (br, 8C; BAr_F *ortho* C*H*), 133.6 (d, ^{1}J(P,C) = 10.6 Hz, 1C; $arom_{phenyl}$ *C*), 133.3 (d, *J*(P,C) = 10.5 Hz, 2C; $arom_{phenyl}$ C*H*), 131.9 (d, *J*(P,C) = 18.7 Hz, 2C; $arom_{phenyl}$ C*H*), 131.0 (2C; $arom_{mesityl}$ C*H*), 130.6 ($arom_{phenyl}$ C*H*), 129.8 ($arom_{phenyl}$ C*H*), 129.8 (d, *J*(P,C) = 7.4 Hz, 2C; $arom_{phenyl}$ C*H*), 129.2 (d, *J*(P,C) = 7.2 Hz, 2C; $arom_{phenyl}$ C*H*), 129.1 ($arom_{mesityl}$ *C*), 129.0

(qq, ^{2}J(F,C) = 31.1 Hz, ^{3}J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 124.7 (q, ^{1}J(F,C) = 272.5 Hz, 8C; BAr_F CF_3), 117.5 (sept, ^{3}J(F,C) = 3.8 Hz, 4C; BAr_F *para C*H), 64.7 (d, ^{2}J(P,C) = 11.1 Hz, 1C; PCH_2CH), 50.6 (NCH_2), 45.9 (d, ^{4}J(P,C) = 5.8 Hz, 1C; NCH_2), 31.9 (d, ^{3}J(P,C) = 5.1 Hz, 1C; $NCH(CH_3)_2$), 28.8 (d, ^{1}J(P,C) = 13.9 Hz, 1C; PCH_2), 21.1 (mesityl CH_3), 19.5 ($NCH(CH_3)_2$), 18.9 ($NCH(CH_3)_2$), 18.5 (br, 2C; mesityl CH_3), 2 $arom_{mesityl}$ *C* not observed;

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$, 295 K) : δ = -26.0 (s);

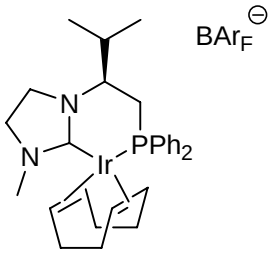
IR (NaCl): $\tilde{\nu}$ = 3067w, 2970w, 2939w, 1639m, 1357m, 1279s, 1126sbr, 998w, 934w, 889m, 839m, 744w, 710m, 675m, 577w, 504w cm^{-1};

MS (FAB): *m/z* (%): 443 (100) $[M - BAr_F]^+$, 459 (32) oxidation during measurement;

EA calcd (%) for $C_{61}H_{48}BF_{24}N_2P$ (1306.80): C 56.07, H 3.70, N 2.14; found: C 55.95, H 3.70, N 2.12.

6.4.6 Synthesis of iridium complexes 121a-c

(*S*)-**[(**η^4-1,5-cyclooctadiene**)**-(1-{1-[(diphenylphosphanyl)-methyl]-2-methyl-propyl}-3-methyl-imidazolin-2-ylidene)iridium(I)]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **121a**



Freshly sublimed NaO*t*Bu (18 mg, 0.192 mmol) was added to a solution of imidazolium salt **109a** (231 mg, 0.192 mmol) and $[(\eta^4$-cod)IrCl$]_2$ (64 mg, 0.096 mmol) in THF (10 ml). The reaction mixture was stirred at room temperature for 2 hours then concentrated *in vacuo* to remove the solvent. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2 to yield a red solid (210 mg, 0.140 mmol, 73%).

$[\alpha]_D^{20}$ = -17 (c = 0.15, $CHCl_3$);

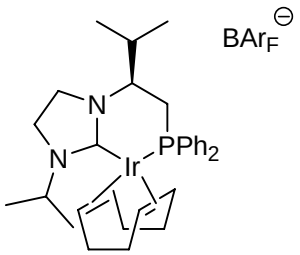
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, CD_2Cl_2, 295 K) : δ = 17.05 (s, 0.75; minor), 16.44 (s, major);

IR (KBr): $\tilde{\nu}$ = 3076w, 2968w, 2887w, 2840w, 1612w, 1526m, 1440m, 1357s, 1279s, 1127s, 998w, 934w, 889m, 838w, 744w, 711m, 674m, 579w, 518w, 479w, 448w cm^{-1};

MS (FAB): *m/z* (%):639 (100) $[M - BAr_F]^+$;

EA calcd (%) for $C_{61}H_{51}BF_{24}IrN_2P$ (1502.02): C 48.78, H 3.42, N 1.87; found: C 48.81, H 3.45, N 1.84.

(*S*)-**[(**η^4-1,5-cyclooctadiene**)**-(1-{1-[(diphenylphosphanyl)-methyl]-2-methyl-propyl}-3-isopropyl-imidazolin-2-ylidene)iridium(I)]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **121b**



Synthesis according to the previous general procedure using imidazolium salt **109b** (291 mg, 0.237 mmol), [(η^4-cod)IrCl]$_2$ (79 mg, 0.118 mmol) and NaO*t*Bu (23 mg, 0.237 mmol) yielded a red solid (250 mg, 0.163 mmol, 69%);

$[\alpha]_D^{20}$ = -5 (c = 0.10, $CHCl_3$);

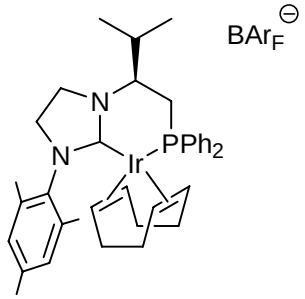
^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2, 295 K) : δ = 15.13 (s, 1.00; major), 14.34 (s, 0.70, minor);

IR (KBr): $\tilde{\nu}$ = 3065w, 2977w, 2886w, 2839w, 1611w, 1491m, 1453m, 1357s, 1279s, 1127s, 999w, 933w, 889m, 839w, 743w, 711m, 675m, 585w, 535w, 524w, 447w cm^{-1};

MS (FAB): *m/z* (%):667 (100) [M - BAr$_F$]$^+$;

EA calcd (%) for $C_{63}H_{55}BF_{24}IrN_2P$ (1530.08): C 49.45, H 3.62, N 1.83; found: C 49.45, H 3.76, N 1.94.

(*S*)-**[(**η^4-1,5-cyclooctadiene**)**-(1-{1-[(diphenylphosphanyl)-methyl]-2-methyl-propyl}-3-methyl-imidazolin-2-ylidene)iridium(I)]-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **121c**



Synthesis according to the previous general procedure using imidazolium salt **109b** (150 mg, 0.115 mmol), $[(\eta^4\text{-cod})IrCl]_2$ (39 mg, 0.057 mmol) and NaO*t*Bu (11 mg, 0.115 mmol) yielded a red solid (138 mg, 0.086 mmol, 75%);

$[\alpha]_D^{20}$ = -6 (c = 0.1, $CHCl_3$);

^{1}H NMR and **^{13}C{^{1}H} NMR** see Figure 6.1

^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 246 K) : δ = 9.91 (s, minor), 6.96 (s, major);

IR (KBr): $\tilde{\nu}$ = 2971w, 2928w, 2888w, 2840w, 1611w, 1486w, 1435w, 1356s, 1278s, 1127s, 1000w, 968w, 935w, 889w, 839w, 744w, 711w, 676m, 580w, 513w, 448w cm^{-1};

MS (FAB): *m/z* (%): 743 (100) $[M - BAr_F]^+$;

EA analysis calcd (%) for $C_{69}H_{59}BF_{24}IrN_2P$ (1606.18): C 51.60, H 3.70, N 1.74; found: C 51.57, H 3.60, N 1.81.

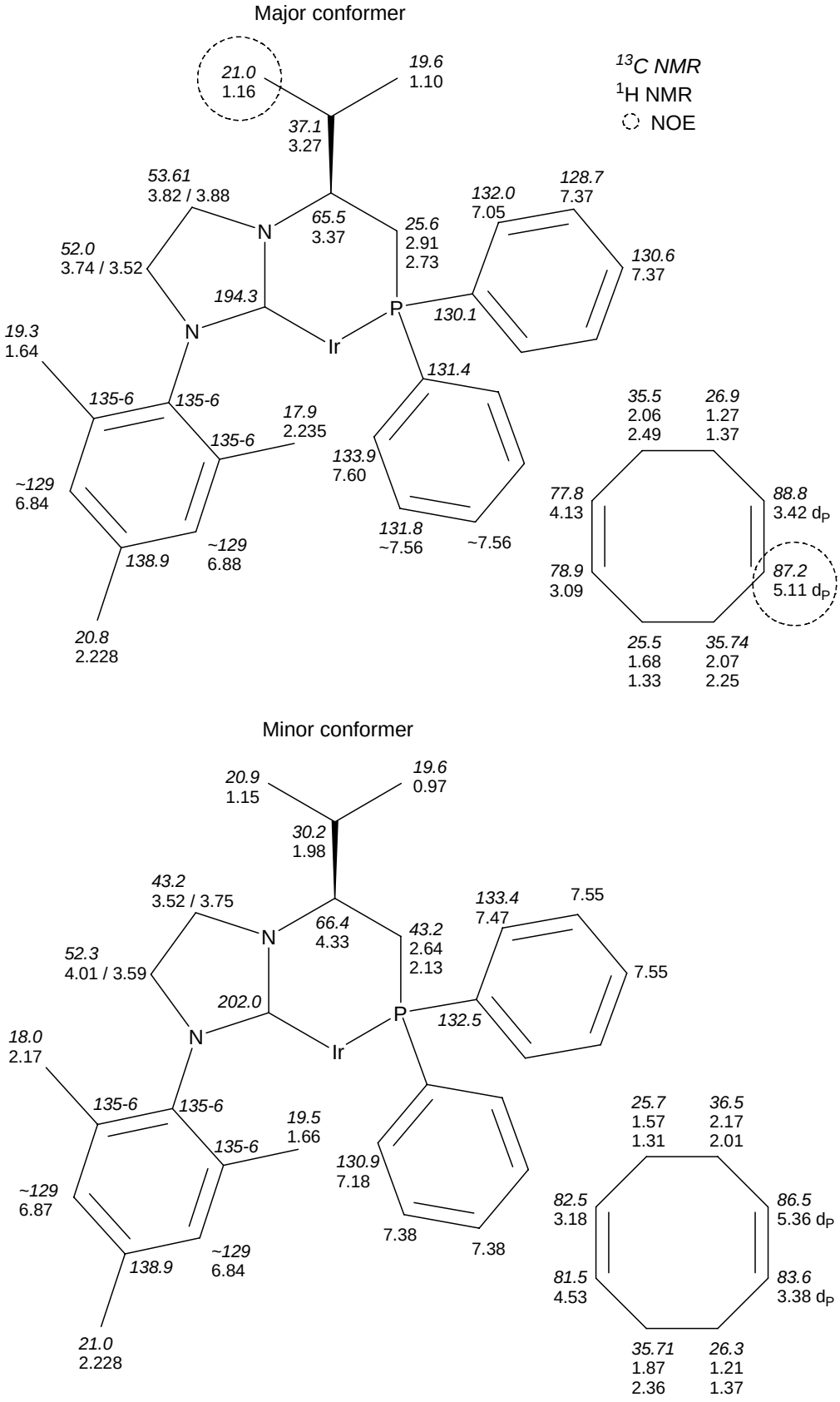
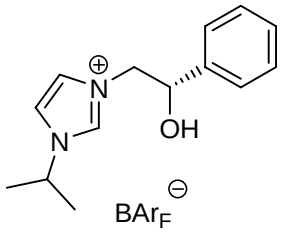


Figure 6.1 ^{1}H-NMR(500.1 MHz, $CDCl_3$, 246 K) and ^{13}C-NMR(125.7 MHz, $CDCl_3$, 246 K) partial assignment of both conformers of complex **121c**. One NOE observed in the major conformer spectrum is crucial for determining the geometry.

6.4.7 Synthesis of imidazolium salt 129

(*R*)-1-(2-hydroxy-2-phenyl-ethyl)-3-isopropyl-3*H*-imidazol-1-ium **129**



A mixture of 1*H*-imidazole (960 mg, 14.1 mmol) and commercially available epoxide **126** (1.693 mg, 14.1 mmol) was heated at 50°C for 12 hours. Degassed CH_3CN (5 ml) and isopropyl iodide (2.39 g, 14.1 mmol) were added to the reaction mixture at room temperature. The solution was heated at 80°C for a further 3 hours. Upon cooling, a solid precipitated from the reaction mixture, was filtered and carefully washed once with CH_3CN (5 ml). Purification by crystallisation from CH_3CN yielded a white solid (1.51 g, 4.23 mmol, 30%).

$NaBAr_F$ (252 mg, 0.285 mmol) was added to a solution of iodide imidazolium salt (102 mg, 0.285 mmol) in CH_2Cl_2 (8 ml). The mixture was filtered and concentrated *in vacuo* to remove the solvent. The crude product was purified by chromatography on silica gel eluting with 5% MeOH in CH_2Cl_2 to yield a colourless oil (260 mg, 0.237, 83%).

$[\alpha]_D^{20}$ = +23.7 (c = 1.00, $CHCl_3$);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 7.89 (mc, 1H; arom C*H*), 7.72 (mc, 8H; BAr_F *ortho* C*H*), 7.54 (mc, 4H; BAr_F *para* C*H*), 7.32 (m, 2H; arom C*H*), 7.11 (m, 2H; arom C*H*), 7.03 (mc, 1H; imid C*H*), 7.01 (mc, 1H; imid C*H*), 5.05 (mc, 1H; C*H*OH), 4.31 (mc, 2H;1 x NCH_2 + 1 x $CH(CH_3)_2$), 4.15 (mc, 1H; NCH_2), 2.32 (br, 1H; O*H*), 1.39 (mc, 6H; $CH(CH_3)_2$), 1H NC*H*N not observed;

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 162.0 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 138.1 (arom *C*), 135.2 (br, 8C; BAr_F *ortho C*H), 133.1 (NCHN), 130.5 (arom C*H*), 130.1 (2C; arom C*H*), 129.4 (qq, ^2J(F,C) = 31.1 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 125.4 (2C; arom C*H*), 124.9 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 124.4 (imid C*H*), 120.1 (imid C*H*), 117.9 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F *para C*H), 72.0 (*C*HOH), 57.3 (NCH_2), 54.5 (*C*H$(CH_3)_2$), 22.82 (CH(*C*$H_3)_2$), 22.78 (CH(*C*$H_3)_2$);

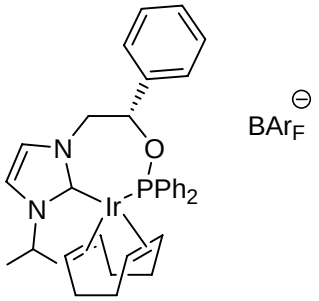
IR (NaCl): $\tilde{\nu}$ = 3645w, 3171w, 3083w, 2992w, 1611w, 1555w, 1461m, 1359s, 1280s, 1120s, 927w, 889m, 834w, 762w, 738w, 710m, 673m, 579w, 528w, 446w cm^{-1};

MS (FAB): *m/z* (%): 231 (100) [M - BAr_F]$^+$;

EA calcd (%) for $C_{46}H_{31}BF_{24}N_2O$ (1094.52): C 50.48, H 2.85, N 2.56, O 1.46; found: C 50.56, H 2.89, N 2.63, O 1.64.

6.4.8 Synthesis of iridium complex 131

(*R*)-**{(**η^4-1,5-cyclooctadiene**)**-[1-(2-diphenylphosphinite-2-phenyl-ethyl)-3-isopropyl-imidazol-2-ylidene]iridium(I)}-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **131**



Phosphamide **130** (80 mg, 0.312 mmol) was added to a homogeneous solution of imidazolium salt **129** (228 mg, 0.208 mmol), 4,5-dichloroimidazole (43 mg, 0.312 mmol) and NEt_3 (32 mg, 0.312 mmol) in CH_2Cl_2 (3 ml) at 0°C. The reaction mixture was stirred at room temperature for 48h. If needed, the reaction can be monitored by ^{31}P-NMR (101.2 MHz, CD_2Cl_2, 300 K) analysis: δ = 115.8 ppm: phosphinite **124**, δ = 58.2 ppm: phosphamide **130** and δ = 17.9 ppm oxidised phosphinite. The solution was concentrated *in vacuo* to remove the solvent and the residue was purified by chromatography on alox (Fluka adjusted to grade III) under inert atmosphere eluting with CH_2Cl_2 to yield an oil (160 mg, 0.124 mmol, 60%).
NaO*t*Bu (12 mg, 0.124 mmol) and [(η^4-cod)IrCl]$_2$ (41.6 mg, 0.062 mmol) were added to a solution of phosphinite **124** (160 mg, 0.124 mmol) in THF (5 ml). The reaction mixture was stirred at room temperature for 2 hours. The solution was concentrated *in vacuo* to yield a red solid. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2 to yield a red product (135 mg, 0.086 mmol, 69%).

$[\alpha]_D^{20}$ = +33 (c = 0.10, $CHCl_3$);

^{1}H NMR and **^{13}C{^{1}H} NMR** see Figure 6.2

^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 300 K) : δ = 96.5 (s, major), 86.8 (s, major);

IR (KBr): $\tilde{\nu}$ = 2955w, 2924w, 2894w, 2848w, 1611w, 1453m, 1358s, 1280s, 1114s, 933w, 887m, 837w, 756w, 709m, 675m, 581w, 491w, 447w cm^{-1};

MS (FAB): *m/z* (%):715 (100) [M - BAr$_F$]$^+$;

EA calcd (%) for $C_{61}H_{51}BF_{24}IrN_2PO$ (1578.08): C 50.23, H 3.26, N 1.78; found: C 50.22, H 3.45,N 1.82.

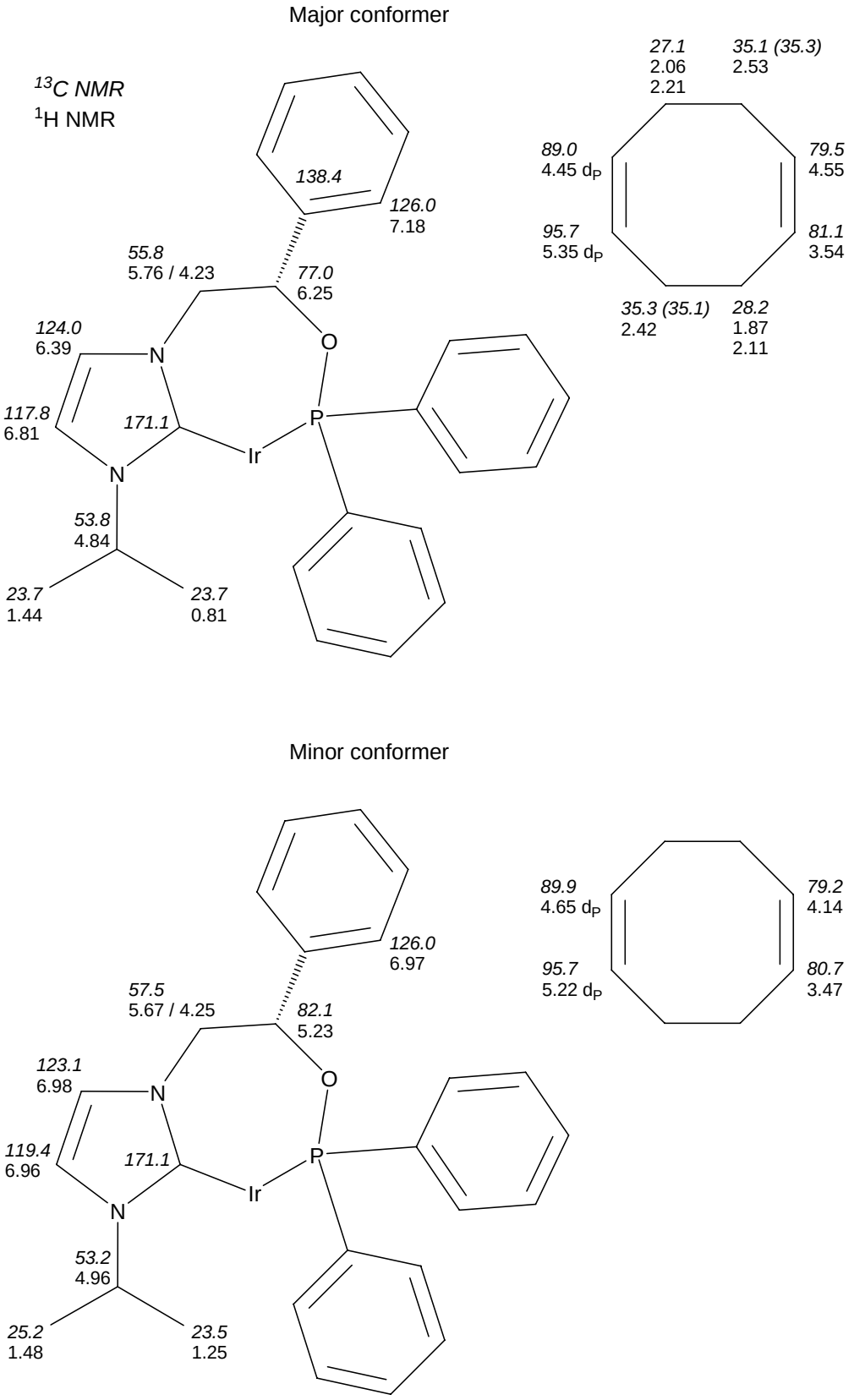
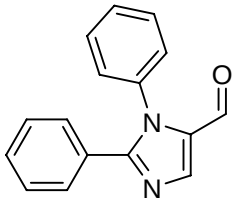


Figure 6.1 ^{1}H-NMR(500.1 MHz, $CDCl_3$, 246 K) and ^{13}C-NMR(125.7 MHz, $CDCl_3$, 246 K) partial assignment of both conformers of complex **131**.

6.4.9 Synthesis of aldehyde 139

2,3-diphenyl-3*H*-imidazole-4-carbaldehyde **139**



K_2CO_3 (2.11 g, 15.3 mmol) was added to a solution of *N*-phenylbenzamidine **138** (2.00 g, 10.2 mmol) and bromoaldehyde **137** (2.95 g, 15.3 mmol) in a mixture of CH_3Cl and H_2O (8:1, 22.5 ml) at room temperature. The reaction mixture was stirred at room temperature for 10 hours. Water (100 ml) and CH_2Cl_2 (100 ml) were added to the mixture. The organic layer was separated and the aqueous layer was extracted two times with CH_2Cl_2 (2 x 100 ml). The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated *in vacuo* to remove the solvent. The residue was purified by chromatography on silica gel eluting with 5% CH_3CN in CH_2Cl_2 to yield a white solid (1.96 g, 7.89 mmol, 77%).

$\boldsymbol{R_f}$ = 0.28 (CH_3CN /CH_2Cl_2 5:95);

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) : δ = 9.64 (s, 1H; C*H*O), 8.02 (s, 1H; NCC*H*N), 7.54-7.43 (m, 3H; arom C*H*), 7.42-7.37 (m, 2H; arom C*H*), 7.37-7.22 (m, 5H; arom C*H*);

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K) : δ = 178.8 (*C*HO), 152.9 (*C*), 141.3 (*C*H), 136.5 (*C*), 134.1 (*C*), 130.2 (*C*H), 130.0 (2C; arom *C*H), 129.9 (*C*H), 129.5 (2C; arom *C*H), 128.9 (*C*), 128.0 (2C; arom *C*H), 128.1 (2C; arom *C*H);

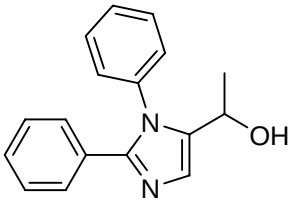
IR (KBr): $\tilde{\nu}$ = 3058w, 2924w, 2846w, 1677s, 1525m, 1496m, 1458m, 1438m, 1421m, 1339m, 1289m, 1267m, 1170m, 1074w, 1027w, 954w, 926w, 887w 815m, 780m, 722m, 696m, 558m cm^{-1};

MS (FAB): *m/z* (%): 249(100) $[M + H]^+$;

EA calcd (%) for $C_{16}H_{12}N_2O$ (248.28): C 77.40, H 4.87, N 11.28, O 6.44; found: C 77.42, H 4.79, N 11.43, O 6.48.

6.4.10 Synthesis of alcohol 140

1-(2,3-diphenyl-3*H*-imidazol-4-yl)-ethanol **140**



A 3M solution of MeMgCl (2.82 ml, 8.46 mmol) in THF was added to a solution of aldehyde **139** (1.40 g, 5.63 mmol) in THF (50 ml) at -78°C. The reaction was stirred for ½ hour and warmed to room temperature. After stirring for 12 hours, a saturated aqueous solution of NH_4Cl was added until the formation of two phases. The organic layer was separated and the aqueous layer was extracted three times with Et_2O (3 x 50 ml). The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated *in vacuo* to remove the solvent. The residue was purified by crystallisation from hot AcOEt to yield white crystals (1.25 g, 4.73 mmol, 83%).

$\boldsymbol{R_f}$ = 0.39 (EtOAc);

m.p. 167-168°C;

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.41 (mc, 3H; phenyl C*H*), 7.32-7.15 (m, 6H; 7 x phenyl C*H* + 1 x imid C*H*), 4.59 (q, ^3J(H,H) = 6.6 Hz, 1H; C*H*OH), 3.08 (br, 1H; O*H*), 1.50 (d, ^3J(H,H) = 6.6 Hz, 3H; CH_3), 2 arom. H have very broad signal in the aromatic region and are not assigned;

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 148.0 (*C*), 138.3 (CH_3CHC), 137.1 (*C*), 130.2 (*C*), 129.6 (2C; phenyl *C*H), 129.0 (phenyl *C*H), 128.5 (2C; phenyl *C*H), 128.4 (phenyl *C*H), 128.3 (br, 2C; phenyl *C*H), 128.2 (2C; phenyl *C*H), 125.6 (imid *C*H), 60.8 (*C*HOH), 22.3 (CH_3);

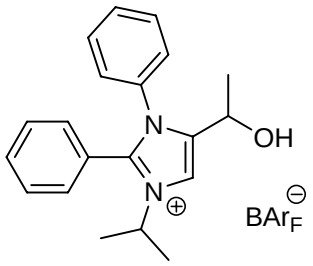
IR (KBr): $\tilde{\nu}$ = 3226mbr, 3061m, 2977m, 2884w, 2364w, 1597w, 1499m, 1462m, 1403m, 1362w, 1282w, 1158w, 1118m, 1072m, 957w, 896w, 829w, 776m, 698m cm^{-1};

MS (FAB): *m/z* (%): 265 (100) $[M + H]^+$;

EA calcd (%) for $C_{17}H_{16}N_2O$ (264.32): C 77.25, H 6.10, N 10.60, O 6.05; found: C 76.99, H 6.08, N 10.59, O 6.16.

6.4.11 Synthesis of imidazolium salt 141

4-(1-hydroxy-ethyl)-1-isopropyl-2,3-diphenyl-3*H*-imidazol-1-ium-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **141**



*i*PrI (322 mg, 1.89 mmol) was added to a solution of alcohol **140** (500 mg, 1.89 mmol) in DMF (1.5 ml). The reaction mixture was heated at 95°C for 18 hours and then concentrated *in vacuo* at 80°C. The residue was purified by chromatography on silica gel eluting first with CH_2Cl_2 and then with 5% MeOH in CH_2Cl_2 to yield an oil. $NaBAr_F$ was added to a solution of the oil in CH_2Cl_2 (5 ml). The solution was stirred at room temperature for 15 minutes, was filtered and concentrated *in vacuo* to remove the solvent. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2 to yield a white solid (420 mg, 0.360 mmol, 19%).

$\boldsymbol{R_f}$ = 0.47 (CH_2Cl_2/MeOH 100:5);

m.p. 147-148°C;

^{1}H NMR (500.1 MHz, $CDCl_3$, 295 K) : δ = 7.70 (mc, 8H; BAr_F *ortho* C*H*), 7.53 (mc, 5H; 4 x BAr_F *para* C*H* + 1 x phenyl C*H*), 7.46 (mc, 1H; phenyl C*H*), 7.43-7.36 (m, 5H; 4 x phenyl C*H*)+ 1 x imid C*H*), 7.16 (mc, 2H; phenyl C*H*), 4.72 (q, ^3J(H,H) = 6.5 Hz, 1H; C*H*OH), 4.47 (mc, 1H; C*H*(CH_3)$_2$), 1.77 (br, 1H; OH), 1.46 (mc, 6H; CH(C*H*$_3$)$_2$), 1.43 (d, ^3J(H,H) = 6.5 Hz, 1H; C*H*$_3$), 2 arom. H have very broad signal in the aromatic region and are not assigned;

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 295 K) : δ = 161.8 (q, ^1J(B,C) = 49.9 Hz, 4C; BAr_F quat. *C ipso* to B), 145.5 (N*C*N), 140.2 (CH_3CHC), 134.9 (br, 8C; BAr_F *ortho C*H), 133.4 (phenyl *C*H), 131.9 (phenyl *C*), 131.8 (phenyl *C*H), 130.5 (2C; phenyl *C*H), 130.2 (2C; phenyl *C*H), 129.7 (2C; phenyl *C*H), 129.0 (qq, ^2J(F,C) = 31.12 Hz, ^3J(B,C) = 2.9 Hz, 8C; BAr_F *C ipso* to CF_3), 127.2 (br, 2C; phenyl *C*H), 124.7 (q, ^1J(F,C) = 272.5 Hz, 8C; BAr_F *C*F_3), 120.1 (phenyl *C*), 117.53 (sept, ^3J(F,C) = 3.8 Hz, 4C; BAr_F *para C*H), 60.8 (*C*HOH), 52.6 (*C*H(CH_3)$_2$), 22.9 (3C; CH(*C*H$_3$)$_2$), 22.8 (3C; CH(*C*H$_3$)$_2$), 22.0 (*C*H$_3$);

IR (KBr): $\tilde{\nu}$ = 3593w, 3592wbr, 3165w, 3002w, 1611m, 1501m, 1471m, 1357s, 1279s, 1125s, 890m, 838w, 796w, 747w, 712m, 675m, 580w, 448w cm^{-1};

MS (FAB): *m/z* (%): 307 (100) $[M]^+$;

EA calcd (%) for $C_{52}H_{35}BF_{24}N_2O$ (1170.62): C 53.35, H 3.01, N 2.39, O 1.37; found: C 53.29, H 3.03, N 2.40, O 1.45.

6.4.12 Synthesis of phosphinite-imidazolium salt 135

Phosphamide **130** (66 mg, 0.256mmol) was added to a homogeneous solution of imidazolium salt **141** (200 mg, 0.171 mmol), 4,5-dichloroimidazole (35 mg, 0.256 mmol) and NEt_3 (26 mg, 0.256 mmol) in CH_2Cl_2 (3 ml) at 0°C. The reaction mixture was stirred at room temperature for 48h. If needed, the reaction can be monitored by ^{31}P-NMR (101.2 MHz, CD_2Cl_2, 300 K) analysis: δ = 111.3 ppm: phosphinite **135** and δ = 58.2 ppm: phosphamide **130**. The solution was concentrated *in vacuo* to remove the solvent and the residue was purified by chromatography on alox (Fluka adjusted to grade III) under inert atmosphere eluting with a mixture of pentane and CH_2Cl_2 (6:4) to yield a colourless oil (210 mg, 0.155 mmol, 91%).

Since phosphinite **135** is an air-sensitive compounds, every attempts to synthesise C(5) activated NHC iridium complex was performed with freshly prepared phosphinite imidazolium salt **135**.

6.5 X-ray data analyses

X-ray data analyses were carried out by Mr Markus Neuburger at the Departement of Chemistry at the University of Basel. The crystal structures were solved by Mr Markus Neuburger, Dr Sylvia Schaffner and Dr Stefan Kaiser.

Single crystals suitable for X-ray analysis were obtained for compounds **62**, **65**, **67**, **81b**, **90p**, **90q**, **122b** and **122c**. Data collection was performed with a Kappa CCD diffractometer. The structures were solved with SIR92[4] or SIR97 and refined with CRYSTALS.[5] A Chebychev polynomial was applied as a weighting scheme.[6] Hydrogen atoms were calculated and refined as riding atoms.

Despite of unsatisfactorily refinements, structure **62** and **67** were used in this work.

It is out of doubt that the postulated carbene-complex is present in structure **62**. However refinement presented problems and the R-value remained at 6.4%. Difference Fourier maps still show quite high maxima, most of them near the cod-ligand, which could not be explained and modelled using a disorder model. It is therefore possible that the crystal was a twin or that it contains crystalline impurities causing errors in the data. The structure is good enough to show clearly the coordination geometry and the connectivity of the synthesised compound, but crystallographic data such as bond lengths and angles can not be used.

The asymmetric unit of the structure of **67** contains two cations and two anions. Both iridium complexes show the same configuration, but fitting one model on top of the other shows differences in conformation. If the arrangement is pseudo-centrosymmetric, all non-chiral parts would fit the higher symmetry in such a way that the structure solves (to some extent) in the controsymmetric spacegroup P 21/n. Reflections measured at low Theta angles had to be omitted in order to refine successfully (errors due to the effects of the beam stop). Otherwise the pseudo-symmetric arrangement caused some temperature parameters of the carbon atoms of the cod ligand to refine to values that were not physically sensible. The following difference Fourier map showed rather high residual electron density, most maxima were found near the iridium atoms. Carrying out absorption correction using DIFABS reduced the maxima, but the electron density that could not be modelled is still too high to get a good R-value. The refinement converged at about 6.9%. The structure gives clear answers to questions about connectivity and conformation of the compound, but crystallographic data such as bond lengths and angles can not be used.

The crystallographic data of complexes **65**, **81b**, **90p**, **90q**, **122b** and **122c** are depicted in Tables 6.1, 6.2 and 6.3.

Table 6.1 Crystallographic data of **65** and **81b**.

Complex	**65**	**81b**
Molecular Formula	$C_{27}H_{34}Cl_1Ir_1N_2$	$C_{54}H_{47}B_1F_{24}Ir_1N_3O_1$
Formula Weight	614.25	1412.97
Colour	orange	orange
Temperature (K)	293	173
Crystal size (mm^3)	0.23 x 0.28 x 0.32	0.30 x 0.30 x 0.38
Crystal system	orthorhombic	monoclinic
Space group	P 2_1 2_1 2_1	P 2_1
a (Å)	11.7124(2)	10.8046(2)
b (Å)	12.4049(3)	19.6132(5)
c (Å)	16.6848(3)	13.9118(3)
α (Å)	90	90
β (Å)	90	111.2951(19)
γ (Å)	90	90
Volume ($Å^3$)	2424.15(8)	2746.8
Z	4	2
Density (calc.)($Mg\ m^{-3}$)	1.683	1.708
μ (Mo K_α) (mm^{-1})	5.636	2.555
Θ_{max} (°)	30.029	32.51
Reflections measured	38620	75698
Reflections independent	7071	19214
Reflection used	3993(>4.00σ(I))	14183 (>3.00σ(I))
Number of parameters	335	859
R (observed data)	0.0265	0.0313
wR (all data)	0.0342	0.0302
Goodness of fit on F	1.0974	1.0147
Residual density (e $Å^{-3}$)	-1.14/0.77	-1.15/1.76
CCDC deposition code		288265

Table 6.2 Crystallographic data of **90p** and **90q**.

Complex	**90p**	**90q**
Molecular Formula	$C_{62}H_{48}B_1F_{24}Ir_1N_3O_2$	$C_{22}H_{35}F_6Ir_1N_3O_1P_1$
Formula Weight	1527.06	694.72
Colour	orange	red
Temperature (K)	173	173
Crystal size (mm^3)	0.11 x 0.16 x 0.19	0.24 x 0.30 x 0.33
Crystal system	orthorhombic	orthorhombic
Space group	P $2\ 2_1\ 2_1$	P $2_1\ 2_1\ 2_1$
a (Å)	12.5922(15)	11.903(1)
b (Å)	18.6153(14)	14.1273(15)
c (Å)	26.563(3)	14.8258(11)
α (Å)	90	90
β (Å)	90	90
γ (Å)	90	90
Volume ($Å^3$)	6226.6(11)	2493.1
Z	4	4
Density (calc.)($Mg\ m^{-3}$)	1.709	1.851
μ (Mo K_α) (mm^{-1})	2.268	5.485
Θ_{max} (°)	27.501	35.00
Reflections measured	188493	46765
Reflections independent	14273	10907
Reflection used	10804 (>2.00σ(I))	9941(>2.00σ(I))
Number of parameters	1056	309
R (observed data)	0.0432	0.0278
wR (all data)	0.0401	0.0266
Goodness of fit on F	1.0496	1.0348
Residual density ($e\ Å^{-3}$)	-1.60/2.96	-2.90/1.56
CCDC deposition code	288266	288267

Table 6.3 Crystallographic data of **122b** and **122c**.

Complex	**122b**	**122c**
Molecular Formula	$C_{31}H_{43}B_1F_4Ir_1N_2P_1$	$C_{37}H_{47}B_1F_4Ir_1N_2P_1$
Formula Weight	753.29	829.72
Colour	orange	orange
Temperature (K)	173	173
Crystal size (mm^3)	0.20 x 0.22 x 0.24	0.16 x 0.20 x0.22
Crystal system	monoclinic	monoclinic
Space group	P 1 2_1 1	P 1 2_1 1
a (Å)	9.61460(10)	10.16900
b (Å)	15.13960(10)	10.97560(10)
c (Å)	11.07970(10)	15.4379(2)
α (Å)	90	90
β (Å)	110.3712(5)	91.4016(4)
γ (Å)	90	90
Volume ($Å^3$)	1511.91(2)	1722.52(3)
Z	2	2
Density (calc.)($Mg\ m^{-3}$)	1.655	1.600
μ (Mo K_α) (mm^{-1})	4.517	3.973
Θ_{max} (°)	32.600	32.545
Reflections measured	21652	84111
Reflections independent	10991	12477
Reflection used	10142(>3.00σ(I))	11463(>3.00σ(I))
Number of parameters	362	417
R (observed data)	0.0202	0.0212
wR (all data)	0.0238	0.0257
Goodness of fit on F	1.0632	0.8594
Residual density (e $Å^{-3}$)	-2.85/2.24	-2.40/2.41
CCDC deposition code		

6.6 Bibliography

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March 2001 – July 2001 **Diploma work** at Firmenich Research and Development centre, Geneva, Switzerland under the supervision of **Prof. Carlo Floriani** and **Dr. Denis Jacoby**. "Michael addition catalysed by copper: Access to fragrance and flavour derivatives"

Award: *Ciba Speciality Chemicals* prize for the best diploma work.

Oct. 1997 – July 2001 **Chemistry undergraduate course** at the University of Lausanne, Switzerland.

A theoretical and practical education with a heavier emphasis on organic chemistry and inorganic chemistry.

Experimental work under the supervision of **Prof. Geoffrey Bodenhausen**; a one semester research project using NMR spectroscopy to investigate the structure of proteins in liquid phase.

Experience

Since Oct. 2002 **Supervision** of two final year undergraduate students.

Laboratory supervisor for the 2nd year "*Organic Chemistry*" course.

Oct. 1999 – July 2001 **Chemistry section representative**

Communicating between the student body and staff on issues concerning the running of the section.

July 2000 – Sept. 2000 **Three months placement in Industry, Firmenich Research and Development centre**, Geneva, Switzerland.

July 1999 – Sept. 1999 **Summer undergraduate research student**, at the Laboratory of Polyelectrolytes and BioMacromolecules of the Swiss Federal Institute of Technology (EPFL), Switzerland under the supervision of Prof. D. Hunkeler.

Skills and Specialist Training

Languages	French (native language), fluent in English and German, basic knowledge in Italian.
Organic Chemistry	Multi-step organic synthesis, catalysis (metal-catalysed, chiral ligand design) and Schlenk techniques.
Analytical Chemistry	NMR, HPLC (including chiral and semi-preparative) and GC (including chiral).
Computing and Software	Microsoft Office Suite, Chemistry Software (ISIS suite, Sci-Finder, X-WIN NMR) and webpage design (design of the Pfaltz's group webpage with Macromedia Dreamweaver).

Publications

"Synthesis and Application of Chiral N-Heterocyclic Carbene-Oxazoline Ligands: Ir-Catalyzed Enantioselective Hydrogenation"
Nanchen Steve, Pfaltz Andreas, *submitted.*

"Accurate Measurement of Residual Dipolar Couplings in Anisotropic Phase"
Cutting Brian, Tolman Joel R., **Nanchen Steve**, Bodenhausen Geoffrey, *Journal of Biomolecular NMR* **2002**, *23*, 195-200.

The diploma work results are included in:
"Process and Catalysts for the Preparation of Michael-Reaction Adducts"
Firmenich SA, Switzerland, *Eur. Pat. Appl.* **2002**, EP 6,686,498, 11pp.

Conferences and Courses Attended

July 2005	OMCOS-13, Geneva, Switzerland – Poster presentation
May 2005	Organometallic Chemistry and its Application to Organic Synthesis 4 Day Graduate Course given by Prof. Stephen L. Buchwald and Prof. Eric N. Jacobsen.
October 2004	Fall Meeting of the Swiss Chemical Society, Zürich – Poster presentation
October 2003	Fall Meeting of the Swiss Chemical Society, Lausanne – Poster presentation
July 2003	OMCOS-12, Toronto, Canada – Poster presentation

Activities

Sports	Mountaineering and climbing. Member of the Swiss Alpine Club for nine years. **Mountaineering guide** trained to take groups of children and young adults, since 1997.

Reference

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Eidesstattliche Erklärung

Ich erkläre, dass ich die Dissertation "*N*-Heterocyclic Carbene Ligands for Iridium-Catalysed Asymmetric Hydrogenation" nur mit der darin angegebenen Hilfe verfasst und bei keiner anderen Universität und keiner anderen Fakultät der Universität Basel eingereicht habe.

Basel, den 3. September 2005 Steve Nanchen